

Physical apparatus parameters and model for vibrating tube densimeters at pressures to 140 MPa and temperatures to 473 K

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Abstract

Vibrating tube densimeters are well-established tools for measuring fluid densities precisely at elevated temperatures and pressures. However, the conventional method of calibrating them utilises a model in which the apparatus parameters are represented as polynomials of temperature and pressure that contain a variable number of terms. Here a robust, physically-based model is presented and demonstrated for six different instruments at temperatures from (273 to 473) K, pressures from (0 to 140) MPa and densities from (0 to 1050) kg m⁻³. The model's physical basis ensures that only seven apparatus parameters are required to relate the measured resonant period to fluid mass density with an average r.m.s. deviation of ± 0.23 kg m⁻³ across all six densimeters. Estimates for each of the apparatus parameters were made based on the geometry and material properties of the vibrating tubes, and these estimates were consistent with the parameter values determined by calibration with reference fluids. Three of the apparatus parameters describe the temperature dependence of the resonant period: for the six vibrating tubes tested, the relative standard deviations of these parameters were all within the range of values estimated from the thermoelastic properties of the Hastelloy tubes. Two distinct parameters are required to describe the pressure dependence of the vibrating tube's volume and effective spring constant, both of which are estimable from equations describing the elastic deformation of thick-walled tubes. The extensive calibrations conducted demonstrate that, for these densimeters, the variations with pressure of the tube's spring constant and its volume have a ratio that is neither 0 nor 1, as has been assumed previously. The model's physical basis allows vibrating tube densimeters to be calibrated accurately using fewer reference fluid measurements than required by the conventional method. Furthermore, use of the physically-based model reduces the uncertainty of measurements made at densities, temperatures or pressures beyond the range of the calibration.

Introduction

Vibrating tube densimeters (VTDs) have been used widely for over 30 years to determine the density of fluids, with many designs reported in the literature for operation at high pressures and temperatures¹. Several commercial suppliers provide vibrating tube densimeters to many industries for multiple applications (e.g. refs. 2 and 3) because they provide a rapid and robust means of measuring the density of a wide range of gases and liquids. The precision achievable with a VTD is excellent and can often be limited by the ability to control the temperature, pressure or composition of the sample: typically densities can be measured with a precision of $\pm 0.01 \text{ kg m}^{-3}$, which for aqueous liquids corresponds to a relative precision of 10 parts per million.¹

In general a VTD consists of a hollow tube that has been bent into a 'U' or 'V' shape and which, for purposes of making a measurement, is filled with the fluid sample of interest. The U shape allows the tube's fundamental bending mode to be excited and monitored using wire-coil electromagnets mounted on or near the tube¹. Measurement of the VTD's resonance period, τ , can be related to the mass density of the fluid, ρ_F , contained within the tube at pressure, p , and temperature, T , by means of the relation

$$\rho_F(p, T) = A(p, T)\tau^2 - B(p, T). \quad (1)$$

Here, A and B are apparatus parameters specific to the VTD being used, which vary with temperature and pressure and which must be determined by calibration through measurements of the resonance period when the VTD is evacuated and/or filled with reference fluids. Such relative density measurements are conducted in one of two ways. Either the reference calibration fluid is used to determine the values of A and B at (almost) exactly the same (p, T) condition at which the sample fluid's density is to be determined as described, for example, by Morrison and Ward.⁴ Alternatively calibration measurements are made with the reference fluid over a range of conditions to establish how A and B vary with pressure and temperature sufficiently well, so that the sample fluid density can be determined reliably over a similar (but not identical) range of conditions. Both approaches require that the apparatus parameters are sufficiently stable that they do not change over the time between calibration and sample measurement; however this requirement is more stringent for the latter approach if it is to be useful. For many applications and VTDs this requirement is met, in which case the second approach can significantly reduce amount of time and effort spent calibrating the VTD if sample measurements need to be measured over a wide range of pressures and temperatures. Of course, in such cases the stability of the calibration should be checked sufficiently often to ensure that inadvertent changes in the apparatus parameters have not occurred, particularly if the sample fluids are chemically aggressive or able to deposit solids.

Ideally, the calibration measurements used to determine $A(p, T)$ and $B(p, T)$ should cover a range of temperature, pressure and reference fluid density that encompasses the intended range of conditions to be measured for the unknown fluid. Under those circumstances, the particular model used for the (p, T) dependence of the apparatus parameters is not critical as long as it varies smoothly over the calibrated range because it is being used for interpolation. As suggested by a leading manufacturer,⁵ power series expansions in temperature and pressure are a common choice for the functional forms of $A(p, T)$ and $B(p, T)$:

$$A(p, t) = \sum_{i=0}^N \sum_{j=0}^M a_{ij} t^i p^j, \quad (2)$$

$$B(p, t) = \sum_{i=0}^n \sum_{j=0}^m b_{ij} t^i p^j. \quad (3)$$

Here, $t = T - T_0$, where T_0 is a reference temperature (which if chosen to be 273.15 K makes t the temperature in °C), and the coefficients a_{ij} and b_{ij} are determined by regression of Eq. (1) to the reference fluid densities. There are some problems with this approach, however, such as determining the values of n , m , N and M , which determine the highest order dependencies on pressure and temperature. In addition, it can be difficult to establish whether all the terms in these equations are necessary. The extent of the summations is related to the (p, T) range over which the calibration is conducted, and statistical tests can help identify significant and correlated terms. However, these guiding considerations can only be of assistance so far because, for example, statistical tests cannot adequately resolve whether a linear pressure dependence should be included in both A and B , just B , or just A .

Furthermore there are circumstances, such as the measurement of brine densities^{6,7}, for which appreciable extrapolation of the model used to describe the VTD is required beyond the range of the typical reference fluid (water) calibration. In that case, if the data being measured are to be converted to accurate densities, it is vital to ensure the apparatus model and the parameters therein are well linked to quantities that are representative of the VTD's physical properties. Thus, while use of Eqs. (2) and (3) can be sufficient for interpolation, such an approach is far from ideal in a general sense because (a) any extrapolation has limited reliability, (b) extensive/excessive calibrations with reference fluids are required, (c) the parameters a_{ij} and b_{ij} are not readily linked to physical properties of the apparatus, and (d) it can be difficult to determine whether or not the model is over parameterised. Accordingly it would be desirable to develop an alternative model of a VTD apparatus in which the parameters determined by regression could be directly compared with, or even constrained to, physically reasonable values.

Many models have been proposed in the literature for the temperature and pressure dependence of the VTD apparatus parameters. None of these, however, have been tested over the wide range of conditions considered in this work, namely pressures to 140 MPa and temperatures from 273 to 473 K. In 1992 Lagourette et al.⁸ and Sousa et al.⁹ independently described methods for calibrating VTDs supplied by Anton Paar, including the model DMA 512 which is a stainless steel VTD operable at pressures to 40 MPa and temperatures to 423 K. These calibration methods involved the determination of the evacuated tube's resonance period as a function of temperature and the use of an assumption regarding the pressure dependence of A or B , which was informed by a physical model of the vibrating tube. In one method⁸, only B was assumed to vary (linearly) with pressure whereas in the second method^{8,9} A and B were assumed to have the same pressure coefficient so that the ratio A/B was independent of pressure. Lagourette et al.⁸ found the first method resulted in a calibration that represented the reference fluid densities slightly better, although the second method has a more physical basis (as will be seen below).

Chang and Moldover¹⁰ presented a custom VTD that could be operated at temperatures to 573 K and pressures to 20 MPa, which they calibrated by monitoring the third harmonic of the tube under vacuum and when filled with water. The novel use of the third harmonic eliminated the need for a large counter mass upon which the tube is normally mounted in commercial apparatus to help filter external vibrations. Instead of A and B in Eq. (1), the calibration function used by Chang and Moldover¹⁰ was expressed in terms of a spring constant $k = A/B$ and tube volume $v = B$. The spring constant was assumed to be independent of pressure and its temperature dependence was represented by a fourth-order polynomial, while the tube volume was assumed to vary linearly with pressure and as a cubic function of temperature. The assumptions made regarding pressure dependence of the parameters were consistent with the second method described by Lagourette et al.⁸ and Sousa et al.⁹ although many more parameters were used to describe empirically the temperature variation of the apparatus parameters given the much wider range of operating temperature.

Holcomb and Outcalt¹¹ presented a framework for a physically-based model of the VTD, which was intended to link the elastic and thermal properties of the tube material together with its geometry to the parameters A and B . However, the results they presented used a quadratic function of temperature only for A and represented B as a linear function of temperature and pressure; moreover none of the parameter values determined by calibration were presented or compared with the tube's elastic, thermal or geometrical properties. In addition, when deriving their justification of the polynomials used in the calibration function only 'first order' terms were retained as was needed to cover the range $0 < t < 150$ C, $p < 14$ MPa. For the purpose of calibrating a VTD, Holcomb and Outcalt¹¹ measured resonance periods under vacuum and for two reference fluids over the range of conditions.

Bouchot and Richon¹² reviewed the array of methods and functions used to calibrate VTDs, presented a more extensive theoretical analysis of the calibration function, and recommended a calibration procedure that utilised measurements of vacuum and a single reference fluid at the same temperature as the intended sample measurements. The framework utilised by Bouchot and Richon¹² was similar to that presented by Holcomb and Outcalt¹¹ but it retained more terms, and allowed the pressure dependence of the tube's volume to be calculated from the elastic and geometrical properties of the tube. The final model contained only two unknown parameters that were both determined at constant temperature: the resonance period of the evacuated tube and a pressure distortion coefficient for the tube's length. The variation with pressure of the tube's internal radius was calculated using an elastic model. When converted to the form of Eq. (1), the physically-based model of Bouchot and Richon¹² meant that A and B had linear pressure coefficients that were both non-zero and similar but slightly different.

The calibration procedure used by Bouchot and Richon^{12,13} required that each time the VTD temperature was changed, the vacuum resonance period and tube length pressure distortion coefficient were re-determined because the thermal variation of the apparatus parameters was not sufficiently repeatable. Only a single reference fluid was needed to determine the pressure dependence of the apparatus at each temperature because, effectively, relationship between the variation of the A and B with pressure was constrained through the use of the elastic model. Bouchot and Richon¹² demonstrated the performance of their model and it compared with others presented previously in the literature by using an Anton Paar DMA 512 to measure N₂, water and a

refrigerant over the temperature range 253 to 333 K and at pressures to 40 MPa. Their results indicated that while for this particular VTD the variation of the vacuum resonance period with temperature could be reasonably well predicted, its drift with time and/or thermal cycling meant that (re-)calibration at each temperature prior to sample measurement was necessary to achieve the smallest uncertainty possible.

Despite the analysis of Bouchot and Richon¹², Lampreia and Nieto de Castro¹⁴ reverted to the model of Sousa et al.⁹ in which only the tube volume (or B) depends on pressure, motivated by the desire to eliminate any pressure dependence of the vacuum resonance period. This ignores the fact that pressure-induced changes in the tube's geometry result in a variation of the tube's spring constant and, thus, causes the isothermal vacuum resonance period to (effectively) vary with pressure. Lampreia and Nieto de Castro¹⁴ also stated that vacuum resonance periods could not be measured directly with sufficient accuracy because the necessary low pressures could not be achieved in the vibrating tube. Their demonstration of this point, however, relied on the assumption that the VTD spring constant does not depend on pressure. Accordingly they recommended the use of two reference liquids at ambient pressure to determine vacuum resonance period at a given temperature, together with additional measurements of a reference liquid over the (p, T) measurement range to determine the variation of the tube's volume with temperature and pressure. Lampreia and Nieto de Castro¹⁴ applied their calibration method to data measured with a DMA 512 at $T = 298.15$ K and at pressures from (0.1 to 30) MPa, and also to data measured over the ranges $(283 < T / K < 323, 0.1 < p / \text{MPa} < 60)$ with the DMA 512P used by Romani and co-workers¹⁵.

Romani and co-workers¹⁵ themselves used a model for the VTD based on the analysis of Bouchot and Richon¹². However, because they aimed to measure high-density ionic liquids they used three calibration fluids with densities between $(700 \text{ and } 1600) \text{ kg}\cdot\text{m}^{-3}$ to determine the apparatus parameters at each temperature as small deviations from the linearity between ρ_f and τ^2 implied by Eq. (1) can become apparent over sufficiently large density range. As shown by Kayukawa et al.¹⁶, for example, the mass ratio of the vibrating tube to its attached counter weight determines the extent of the non-linearity. Kayukawa et al.¹⁶ described a specialised apparatus in which a DMA 512 was removed from its normal mounting and attached to a 5.5 kg counter weight suspended by springs. The system had a mass ratio of 0.003; the corresponding non-linearity causes a systematic error of less than 0.1 kg m^{-3} for densities below 1100 kg m^{-3} which increases to more than 0.3 kg m^{-3} by 1500 kg m^{-3} . To determine this mass ratio and calibrate the VTD, Kayukawa et al.¹⁶ also used two reference liquids at ambient conditions (water and isooctane) together with measurements of water over the temperature and pressure range of interest.

In this work we present an apparatus model for VTDs, developed by extending the framework presented Holcomb and Outcalt,¹¹ that is similar in several respects to the model presented Bouchot and Richon¹². However, the model presented here does not require determination of apparatus parameters at each measurement temperature and, furthermore, we demonstrate its validity for six VTDs (labelled VTD-1 to VTD-6) over the range $0 < t < 200$ °C, $p < 140$ MPa. All of these VTDs were Hastelloy (HC-276) DMA HP or DMA HPM models supplied by Anton Paar, three of which were rated to 140 MPa and three of which were rated to 70 MPa. These VTDs were developed more recently than the DMA 512 models and, based on the consistency of the apparatus parameters determined by reference fluid calibrations, appear to be significantly more stable with time and/or uniform across several different vibrating tubes. The theoretical framework developed allows the apparatus

parameters to be predicted from the material properties of HC-276 and some limited information about the geometry of the vibrating tubes. These predictions are in good agreement with the values obtained by calibration. We demonstrate that the linear pressure coefficients of A and B are similar but slightly different, and that for these six VTDs the ratio of these pressure coefficients has a consistent value. We conclude by considering the minimum number of measurements and reference fluids required for calibration and the likely uncertainty increase associated with extrapolation of the model.

Physically-based Model

The framework presented by Holcomb and Outcalt¹¹ was based on an analysis of a vibrating rod for which the equation of motion is

$$EI \frac{\partial^4 Y}{\partial Z^4} + \rho_R A \ddot{Y} = 0. \quad (4)$$

Here, Y is the vertical displacement of the tube/rod at position Z , \ddot{Y} is the second time derivative of the vertical displacement, and E , I and ρ_R are the tube's Young's modulus, moment of inertia and mass density, respectively. For a tube of length L , the boundary conditions

$$Y(0) = Y(L) = 0 \text{ and} \quad (5)$$

$$\frac{\partial Y(0)}{\partial Z} = \frac{\partial Y(L)}{\partial Z} = 0, \quad (6)$$

give rise to the eigenvalue equation that determines the resonance condition

$$\cos(k_n L) \cosh(k_n L) - 1 = 0 \quad (7)$$

where k_n is an eigenvalue with $k_1 \cong 4.73004$. Solutions to this equation correspond to the resonance condition of the vibrating tube/rod, with the resonance frequency of the n^{th} mode given by

$$\omega_n^2 = \frac{k_n^4 EI}{L^3 m} \quad (8)$$

The resonance period of the fundamental mode, τ , can be expressed in terms of the mass of the evacuated tube, m_0 , its internal volume, V_i , and the density of the fluid it contains, ρ_F .

$$\tau^2 = \frac{4\pi^2 L^3 m}{k_1^4 EI} = \frac{4\pi^2 L^3 (m_0 + \rho_F V_i)}{k_1^4 EI} \quad (9)$$

By re-arranging this equation to make it explicit in the fluid density

$$\rho_F = \left(\frac{k_1^4 EI}{4\pi^2 V_i L^3} \tau^2 - \frac{m_0}{V_i} \right), \quad (10)$$

and by defining a vacuum resonance period, τ_0 ,

$$\tau_0 = 2\pi \sqrt{\frac{L_0^3 m_0}{k_1^4 EI_0}} \quad (11)$$

we have

$$\rho_F = \frac{m_0}{V_i} \left(\left(\frac{L_{00}^3}{L^3} \right) \left(\frac{E}{E_0} \right) \left(\frac{I}{I_{00}} \right) \left(\frac{\tau}{\tau_{00}} \right)^2 - 1 \right) \quad (12)$$

with τ_{00} being the vacuum period at the reference temperature $t = 0$ °C. Equation (12) indicates that the measurement of squared period ratios provides a quantity that is linear with ρ_F and that the temperature and pressure dependence of the VTD apparatus is set by the variation of E with t , and the change in V_i , L and I with t and p , respectively. It is therefore helpful to define the following functions and coefficients to describe the variation of these geometric and material properties of the tube with temperature and pressure

$$E = E_0 (1 + \varepsilon_1 t + \varepsilon_2 t^2) , \quad (13)$$

$$I = I_{00} (1 + \chi_1 t + \chi_2 t^2 + \beta_I p) , \quad (14)$$

$$L = L_{00} (1 + \alpha_1 t + \alpha_2 t^2 + \beta_L p) , \quad (15)$$

$$V_i = V_{00} (1 + 3\alpha_1 t + 3(\alpha_1^2 + \alpha_2) t^2 + \beta_V p) , \quad (16)$$

$$\rho_{00} = \frac{m_0}{V_{00}} = \frac{\rho_M}{S_{00}} . \quad (17)$$

In equations (13) - (17), ρ_M is the density of the material from which the tube wall is made, S is a dimensionless measure of the VTD's sensitivity (as discussed further below), and the subscript "00" denotes the value of the property when the tube is evacuated and at the reference temperature $t = 0$ °C; the single subscript "0" used with E refers to the reference temperature only because the Young's modulus is assumed not to vary with pressure. We consider only a linear variation with pressure for I , L and V , quantified by the corresponding pressure response coefficients, β , but have retained terms to second order in temperature. The temperature and pressure response coefficients for I , L and V are related by geometry and can be re-expressed in terms of common, underlying coefficients. For example

$$\frac{I}{I_{00}} = \frac{R_{00}^4 (1 + \alpha_1 t + \alpha_2 t^2 + \beta_R p)^4 - r_{00}^4 (1 + \alpha_1 t + \alpha_2 t^2 + \beta_r p)^4}{R_{00}^4 - r_{00}^4} \quad (18)$$

which simplifies to

$$\frac{I}{I_{00}} = 1 + 4\alpha_1 t + (6\alpha_1^2 + 4\alpha_2) t^2 + \frac{4(R_{00}^4 \beta_R - r_{00}^4 \beta_r)}{R_{00}^4 - r_{00}^4} p , \quad (19)$$

where r denotes the internal radius and R the external radius of the tube. Consequently,

$$\chi_1 = 4\alpha_1 \text{ and } \chi_2 = 6\alpha_1^2 + 4\alpha_2 \quad (20)$$

which gives

$$\rho_F = \frac{(\rho_M/S_{00})}{(1+3\alpha_1 t + 3(\alpha_1^2 + \alpha_2)t^2 + \beta_V p)} \left[(1 + (\varepsilon_1 + \alpha_1)t + (\varepsilon_2 + \alpha_2 + \varepsilon_1 \alpha_1)t^2 + (\beta_I - 3\beta_L)p) \left(\frac{\tau}{\tau_{00}} \right)^2 - 1 \right] \quad (21)$$

The compound pressure coefficients β_I and β_V can be expressed in terms of the pressure coefficients associated with the tube's linear dimensions: radii r and R and length L . From Eq. (19) we have

$$\beta_I = \frac{4(R_{00}^4 \beta_R - r_{00}^4 \beta_r)}{R_{00}^4 - r_{00}^4} \quad (22)$$

and, since the vibrating tube is a cylinder, we have

$$\beta_V = 2\beta_r + \beta_L \quad (23)$$

The values of β_r and β_L can be estimated from expressions derived from standard elastic theory to describe the expansion of a tube subject to an internal pressure¹⁷. Holcomb and Outcalt¹¹ assumed thin-walled open tubes were most appropriate but as mentioned by Bouchot and Richon¹² the ratio of the VTD's wall thickness to internal radius does not meet the criterion of < 0.1 , so thick-walled formulae should be used. It is less clear whether the deformation formulae used should be for an open or closed cylinder, although based on the results presented below the latter appears to be a better description. A similar approach can be followed for the estimation of β_R ; however there is some ambiguity here because the mechanical constraints associated with the tube's mounting mean that its outer radius is unlikely to be able to deform freely or in a simple manner, as is assumed in the derivation of the standard formula.

Two quantities characterise how much the resonance period varies in response to the VTD being loaded with a fluid of given density: the density of the tube wall material and the ratio of the tube's external and internal radii. The larger the value of ρ_M , the less sensitive the VTD, while the larger the value of sensitivity parameter, S_{00} , which may be estimated via

$$S_{00} = \frac{r_{00}^2}{R_{00}^2 - r_{00}^2}, \quad (24)$$

the greater the instrument's response. In deriving the Eq (24) from Eq (17) it was assumed that the tube's length is long in comparison with its wall thickness. The precise quality of this approximation is not particularly important, however, as the main purpose of S_{00} is to provide a relative measure of the sensitivities of different VTDs made from the same material. Eq (24) is useful if the objective is to estimate R_{00} and, ultimately, an absolute value of τ_{00} . However, in general this is not necessary for fluid density measurements with VTDs.

Comparison of the magnitudes of the thermal coefficients in Eq (21) allows further simplification without significant loss of generality. For Hastelloy HC-276¹⁸ and stainless steel SS316¹⁹, $|\varepsilon_1 / \alpha_1| > 10$, $|\varepsilon_2 / \alpha_2| > 100$, and $|\alpha_1 / (\alpha_1^2 + \alpha_2)| > 1000$. These ratios suggest that any second order variation with temperature should be retained only for terms involving the tube's elastic properties. Furthermore, since the elastic properties only vary with temperature and their variation is manifest in the vacuum resonance period which can be measured directly over the temperature range of interest, it is convenient to represent τ_0 empirically as a quadratic function of temperature. These considerations lead to the following, seven parameter model which we recommend for wide-ranging calibrations of VTDs.

$$\rho_F = \frac{(\rho_M / S_{00})}{(1 + \alpha_V t + \beta_V p)} \left(\left(\frac{\tau}{\tau_{00} (1 + \varepsilon_{\tau 1} t + \varepsilon_{\tau 2} t^2)} \right)^2 (1 + \beta_\tau p) - 1 \right) \quad (25)$$

A summary and description of the seven apparatus parameters used in this model and how they might be determined is given in Table 1.

Table 1. Summary of the seven VTD apparatus parameters used in Eq. (25) and a description of how each might be determined.

Symbol	Parameter	Determined from
S_{00}	Geometric sensitivity factor of evacuated tube at reference temperature	Reference fluid measurements (set by tube's radius and wall thickness)
τ_{00}	Resonance period of evacuated tube at reference temperature	Vacuum measurements
$\varepsilon_{\tau 1}$	Linear temperature response coefficient of spring constant	Vacuum measurements or material properties estimates
$\varepsilon_{\tau 2}$	Quadratic temperature response coefficient of spring constant	High temperature vacuum measurements or material properties estimates
β_τ	Pressure response coefficient of spring constant	High pressure reference fluid measurements
α_V	Linear temperature response coefficient of tube volume	Reference fluid measurements or material properties estimates
β_V	Pressure response coefficient of tube volume	High pressure reference fluid measurements

The use of seven adjustable parameters within an apparatus model may at first sight give cause for concern in terms, for example, of parameter correlation and/or the ability to determine all seven simultaneously via non-linear regression against reference fluid data. Importantly, however, the parameters can and should be determined in two separate sub-groupings from independent sets of measurements. The three parameters describing the vacuum resonance and its variation with temperature, τ_{00} , $\varepsilon_{\tau 1}$, and $\varepsilon_{\tau 2}$ are determined by *linear* least squares regression to data measured with the evacuated VTD. Consequently it is then only necessary to determine four parameters by non-linear regression to reference fluid data measured at high pressure and over the same temperature range. Additionally, as we show in the following sections, it is possible to estimate and even constrain some of the parameters values and thereby further reduce the number of parameters requiring adjustment in the non-linear regression. In principle the number of parameters

could possibly be reduced further because, as shown by Ledbetter²⁰, there is a relationship between a solid's coefficient of thermal expansion and its modulus of elasticity. Romani and co-workers¹⁵ described the variation of the VTD's modulus of elasticity with a semi-empirical function containing Einstein-type exponentials that potentially might be a better representation of the elastic theory of solids. However, we retain the use of a quadratic function to represent the impact of E and its temperature dependence on τ_0 because (i) it has the same number of parameters as the semi-empirical Einstein function, and (ii) the quadratic parameters are simply obtained from linear regression to vacuum resonance period data.

The physically-based model shown in Eq. (25) is related to the conventional apparatus parameters, A and B in Eq. (1) via the following relations:

$$A = \frac{\rho_{00} (1 + \alpha_V t + (\beta_V + \beta_\tau) p)}{\tau_{00}^2 (1 + \varepsilon_{\tau 1} t + \varepsilon_{\tau 2} t^2)} \quad (26)$$

$$B = \rho_{00} (1 + \alpha_V t + \beta_V p). \quad (27)$$

Independent Physical Estimates of VTD Parameter Values

Six of the seven parameters in Table 1 can be estimated independently from knowledge of the VTD's material properties and either of the following pairs of geometric properties [r_{00} and L_{00}] or [r_{00} and V_{00}]. To determine S_{00} , however, either the empty tube's mass must also be known or the VTD's sensitivity must be measured; this could be done, for example, at ambient conditions using a reference fluid such as water. As shown in Figure 1, ρ_M and S_{00} determine the slope of the VTD's linear relationship between the fluid density and the squared ratio of the tube's resonance periods when fluid-filled and evacuated: the larger ρ_M/S_{00} , the less sensitive the instrument.

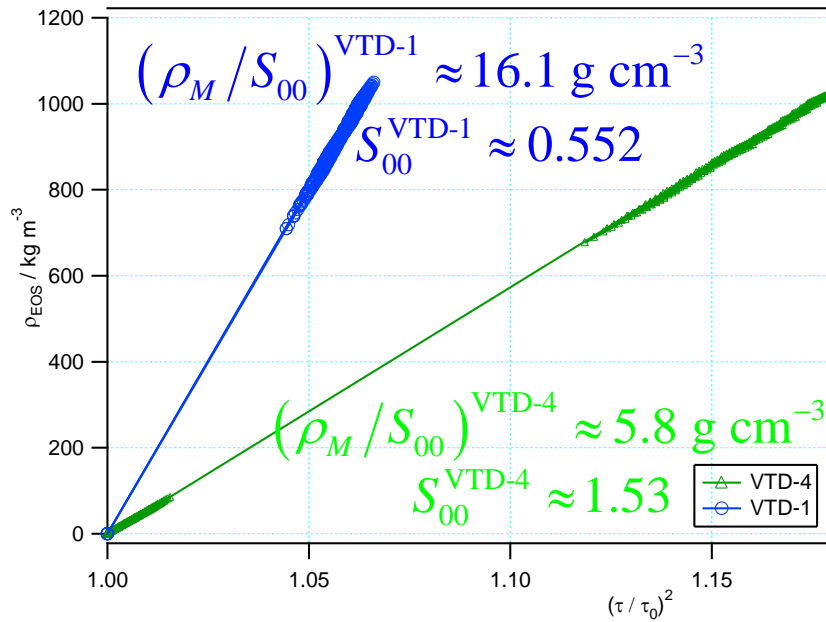


Figure 1. Sensitivities of the two types of VTD used in this work, determined by plotting the equation of state density, ρ_{EOS} , of the reference fluid within the tube against the squared ratio of the resonance period to the

vacuum resonance period, (τ/τ_0) . The slopes of these linear responses determine the sensitivity parameter S_{00} , with VTD-1 (pressure rating of 140 MPa) being 2.8 times less sensitive than VTD-4 (pressure rating of 70 MPa).

From Figure 1 it is clear that VTD-1, which was rated for operation at pressures to 140 MPa, was less sensitive than VTD-4, which was only rated for operation at pressures to 70 MPa. If this measured sensitivity is combined with knowledge of the tube's internal radius and volume then it is possible to estimate τ_{00} . The manufacturer of the VTDs²¹ provided the following information about the Hastelloy VTDs used in this work: all had $r = 1.29$ mm and $V_i = 0.86$ cm³. By assuming the tube's internal volume is geometrically equivalent to that of a cylinder, these values correspond to an effective tube length of 16.5 cm. Using a standard value for the density of Hastelloy¹⁸, Eq (24) can be used to provide an estimate of the tubes external radius, R , and therefore its empty mass. As shown in Table 2 for VTD-1 and VTD-4, this in turn allows the tube's moment of inertia to be determined, and when combined with Young's modulus for Hastelloy¹⁸, an absolute value of τ_{00} to be estimated.

Table 2. Estimates for the two types of VTDs used in this work of the empty tube mass m_0 , external radius R , moment of inertia I , and vacuum resonance period made using the material properties of Hastelloy, manufacturer-specified values of the tube's internal radius and volume, and the measured parameter S_{00} .

	VTD-1	VTD-4
S_{00}	0.552	1.53
m_0 / g	13.9	4.95
$\rho_{\text{Hastelloy}} / \text{g cm}^{-3}$	8.89	8.89
R / mm	2.16	1.66
I / mm^4	15	3.7
$E_{\text{Hastelloy}} / \text{GPa}$	205	205
$\tau_{00} / \mu\text{s}$	1256	1508

The measured values of τ_{00} for VTD-1 and VTD-4 are 2566 μs and 2439 μs , respectively, which are within a factor of two of the values calculated in Table 2. This level of agreement is reasonable considering that the predicted values of the vacuum resonance period made using Eq. (11) are very sensitive to the specified tube length or, equivalently, volume. The measured values of τ_{00} correspond to $V_i = 1.23$ cm³ and 1.09 cm³ for VTD-1 and VTD-4, respectively.

Of more importance to fluid density measurements are estimates of the apparatus temperature and pressure dependence. Comparison of equations (21) and (25) indicates that the temperature dependence of the apparatus is determined by the tube material's linear coefficient of thermal expansion and the temperature dependence its Young's modulus. Specifically, the thermal parameters in eq. (25) can be related to these material properties as follows:

$$\varepsilon_{\tau 1} = \frac{-(\alpha_1 + \varepsilon_1)}{2} \cong \frac{-\varepsilon_1}{2} \quad (28)$$

$$\varepsilon_{\tau 2} = \frac{-(\varepsilon_2 + \alpha_2 + \varepsilon_1 \alpha_1)}{2} \cong \frac{-(\varepsilon_2 + \varepsilon_1 \alpha_1)}{2} \xrightarrow{\text{HC-276}} \varepsilon_{\tau 2} \cong \frac{-\varepsilon_2}{2} \quad (29)$$

$$\alpha_v \cong 3\alpha_1 \quad (30)$$

Equations (28) and (29) indicate that the apparatus parameters $\varepsilon_{\tau 1}$ and $\varepsilon_{\tau 2}$ (for HC-276) correspond to (-1/2) times the coefficients describing the temperature variation of the material's modulus of elasticity. This is a consequence of the choice to express the VTD spring constant's temperature dependence within the denominator of eq. (25); this choice is made because allows $\varepsilon_{\tau 1}$ and $\varepsilon_{\tau 2}$ to be determined directly from linear least squared regression of vacuum period measurements made over a wide temperature range. Values of the apparatus temperature dependence parameters α_v , $\varepsilon_{\tau 1}$ and $\varepsilon_{\tau 2}$ for predicted for the Hastelloy tubes used in this work are listed in Table 3.

To predict the values of β_r and β_v in eq. (25), it is necessary to evaluate the pressure coefficients β_r , β_L , and β_R shown in eqs (22) and (23) for the key tube dimensions, r , L , and R . This can be done using elastic theory and the following formulae for closed, thick-walled tubes¹⁷.

$$\beta_r = \frac{1}{E} \left(\frac{R^2(1+\nu) + r^2(1-2\nu)}{R^2 - r^2} \right) \quad (31)$$

$$\beta_L = \frac{1}{E} \nu \left(\frac{r^2(1-2\nu)}{R^2 - r^2} \right) \quad (32)$$

Here ν is Poisson's ratio, which for HC-276 is 0.307¹⁸. The volume pressure dependence parameter β_v can then be evaluated using eq. (23). To estimate the pressure dependence of the spring constant, β_r , the variation of the tube's outer radius with internal pressure must be estimated. For β_R there is some ambiguity regarding the most appropriate expression to use for its deformation because the tube's outer boundary must be subject to some constraint (likely at its ends) given that it is supported but it cannot be considered completely constrained either given that it is able to vibrate. For the purpose of predicting a physically reasonable value of β_R , one approach to dealing with this ambiguity is to evaluate the two limiting cases:

$$\beta_R = 0 \quad \text{or} \quad \beta_R = \frac{1}{E} \nu \left(\frac{r^2(2-\nu)}{R^2 - r^2} \right) \quad (33)$$

In Eq. (33), the external radius is completely constrained in the first case and completely unconstrained in the second. Using values for β_r , β_L , and β_R calculated using eqs. (31), (32), and (33), respectively, the spring constant's pressure dependence is given by

$$\beta_r = \frac{4(R_{00}^4 \beta_R - r_{00}^4 \beta_r)}{R_{00}^4 - r_{00}^4} - 3\beta_L \quad (34)$$

Values for the pressure dependence coefficients are also listed in Table 3 for VTD-1 and VTD-4, where the two limiting cases for the constraint on the deformation of the tube's external radius of have been used to establish the range over which β_r could be expected to vary.

Table 3. Predicted values for the apparatus temperature and pressure dependence coefficients evaluated using equations (23) and (28)-(34) for VTD-1 and VTD-4 based on their geometry and material properties. The two limiting cases shown in eq.(33), corresponding to complete or no constraints on the external radius' deformation, were used to provide bounds on the spring constant's pressure dependence, β_τ .

	$10^5 \beta_\tau / \text{MPa}^{-1}$	$10^5 \beta_V / \text{MPa}^{-1}$	$10^6 \alpha_V / 3 \text{ K}^{-1}$	$10^6 \varepsilon_{\tau 1} / \text{K}^{-1}$	$10^8 \varepsilon_{\tau 2} / \text{K}^{-2}$
VTD-1, R unconstrained	1.2	3.3	12	130	6
VTD-1, R constrained	-0.95				
VTD-4, R unconstrained	2.7	5.7	12	130	6
VTD-4, R constrained	-5.2				

Results

Apparatus parameters for the three densimeters, VTD-1, VTD-2, and VTD-3, each with a maximum pressure rating of 140 MPa, were determined by calibrations in which their resonance periods were measured under vacuum and/or using a combination of reference fluids over a wide range of temperature and pressure. The seven parameters in eq. (25) were determined in two stages. First τ_{00} , $\varepsilon_{\tau 1}$, and $\varepsilon_{\tau 2}$ were determined by linear least squares regression of vacuum resonance periods measured at various temperatures. For VTD-1, the (t, τ_0) data were measured directly, whereas for VTD-2 and VTD-3 the value of τ_0 at each temperature was determined by extrapolating high-pressure helium measurements to zero pressure (as described below). In the second stage the remaining 4 parameters were determined by non-linear regression of resonance periods measured with the VTD filled with reference fluids to densities calculated from the experimental pressure and temperature using the reference equation of state for those fluids,^{22,23,24,25} all of which were implemented in the software REFPROP 9.0²⁶. For each data point used in the second stage, the measured temperature was used together with the values of τ_{00} , $\varepsilon_{\tau 1}$, and $\varepsilon_{\tau 2}$ determined in the first stage to evaluate the ratio (τ / τ_0) prior to the non-linear regression.

For the three densimeters rated to 140 MPa, the most extensive set of calibration measurements were made for VTD-1. These consisted of 17 measurements under vacuum at 9 temperatures between (273.17 and 447.85) K; 161 measurements of de-ionised water at 7 temperatures between (298.90 and 447.94) K and pressures between (0.26 and 135.30) MPa; and 159 measurements of toluene at 7 temperatures between (298.67 and 448.30) K and pressures between (0.36 and 135.38) MPa. Both the water and toluene were degassed prior to loading into the VTD. The temperature variation for each experimental isotherm was less than 0.03 K, while the measurements at high pressures were each made within a 2 MPa range of one of 17 target pressures separated by about (5 to 10) MPa. The results of the measurements and calibration for VTD-1 are shown in Figure 2, with the best-fit parameters and statistical uncertainties listed in Table 4.

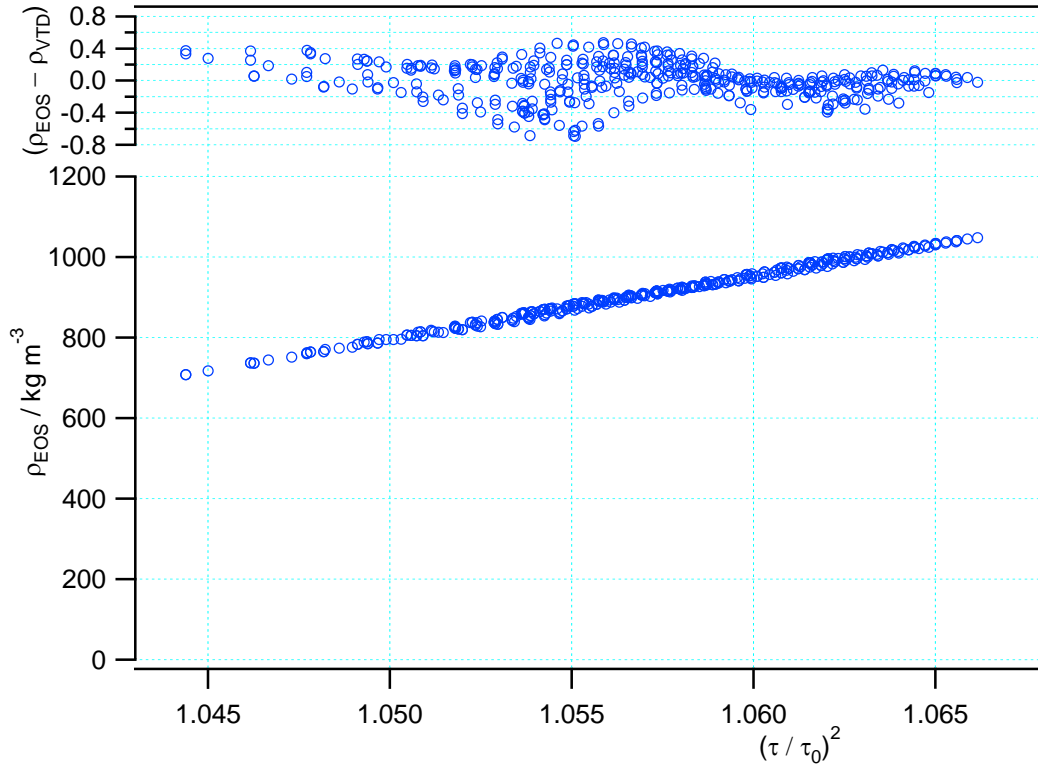


Figure 2. Lower panel: Water and toluene densities calculated using their respective equations of state^{22,23}, ρ_{EOS} , as a function of the squared normalised resonance period $(\tau/\tau_0)^2$ measured for VTD-1. Upper panel: Residuals between the EOS density and the density, ρ_{VTD} , calculated using eq. (25) with the parameters for VTD-1 listed in Table 4.

The regression of the measured vacuum periods to the quadratic function of temperature had a root mean square error (r.m.s.) of $0.0073 \mu\text{s}$. The r.m.s. error of the non-linear regression to the reference fluid densities was $0.22 \text{ kg}\cdot\text{m}^{-3}$, which is comparable to the propagated density uncertainty arising from the uncertainties in the measured temperature, pressure and resonance period of $\pm 0.02 \text{ K}$, $\pm 0.003 \text{ MPa}$, and $\pm 0.02 \mu\text{s}$, respectively.

A similar approach was taken to calibrate VTD-2 and VTD-3, except that no vacuum measurements were made with these two instruments, and supercritical CO_2 was used as the one of the reference fluids instead of toluene. The three sets of reference fluid data consisted of 35 measurements of helium at 5 temperatures between (304.76 and 473.50) K and pressures between (4.91 and 31.51) MPa; 35 measurements of deionised water at 5 temperatures between (304.92 and 473.19) K and pressures between (5.10 and 65.50) MPa; and 27 measurements of CO_2 at 5 temperatures between (304.76 and 473.48) K and pressures between (5.11 and 65.11) MPa. In lieu of making any vacuum measurements for VTD-2 and VTD-3, the resonance periods measured for helium along each isotherm were fit to a quadratic function of pressure, and the constant term in the quadratic was taken to be the vacuum period for that temperature. The results of the measurements and calibrations for VTD-2 and VTD-3 are shown in Figure 3, with the best-fit parameters and statistical uncertainties listed in Table 4.

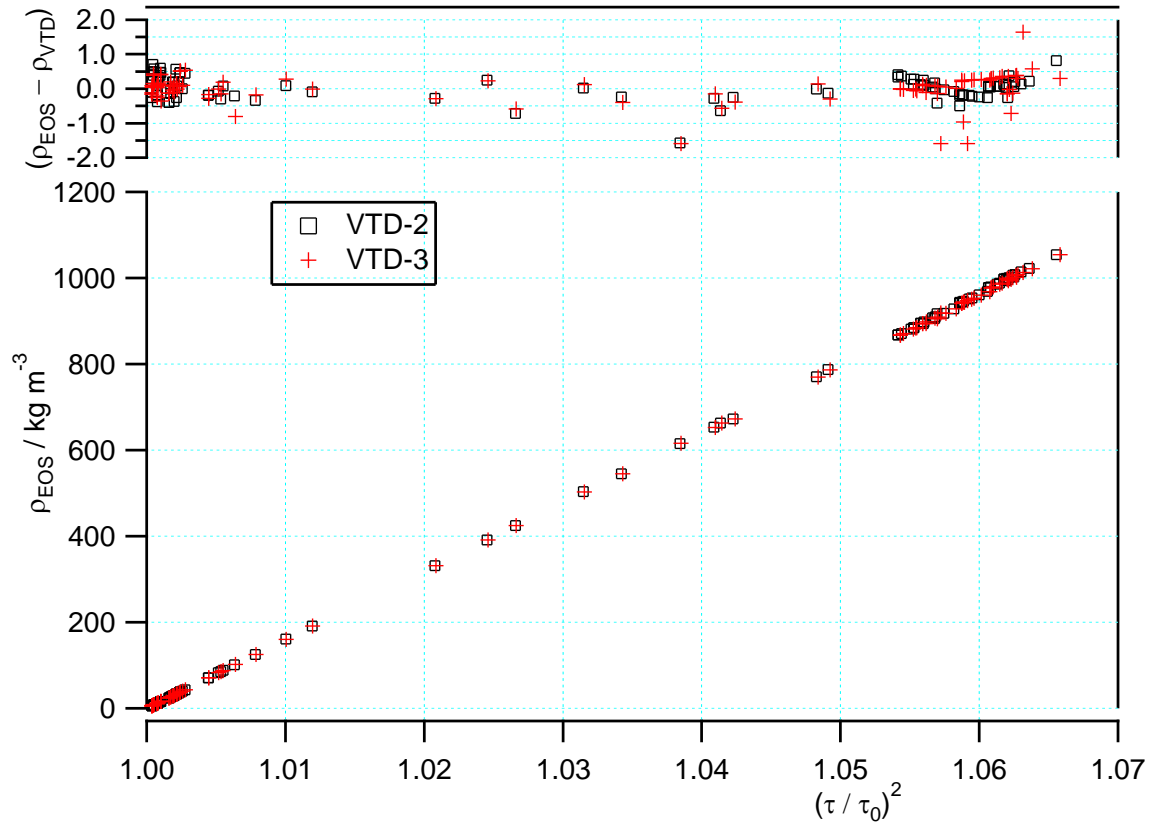


Figure 3. Lower panel: Water, CO₂ and helium densities calculated using their respective reference equations of state^{22,24,25}, ρ_{EOS} , as a function of the squared normalised resonance period $(\tau/\tau_0)^2$ measured for VTD-2 and VTD-3. Upper panel: Residuals between the EOS density and the density, ρ_{VTD} , calculated using eq. (25) with the parameters for VTD-2 or VTD-3 listed in Table 4.

Table 4. Best-fit values for the parameters in eq. (25) determined by calibration to vacuum and/or reference fluid data for VTD-1, -2, and -3, all of which were rated to 140 MPa. The absolute and relative r.m.s. errors of the best fits to each calibration data set are listed, as are the averages of each parameter across the three VTDs. The subscript numbers listed in parentheses correspond to the statistical uncertainty of either the best-fit value or the standard deviation of the averaged values. The (range of) value(s) of each parameter predicted using equations (11), (23) and (28)-(34) are listed for comparison.

Parameter	VTD-1	VTD-2	VTD-3	<VTD> ₁₋₃	PREDICTION
S_{00}	0.552388 ₍₁₄₎	0.549715 ₍₇₅₎	0.551776 ₍₉₆₎	0.5513 ₍₁₄₎	
$\tau_{00} / \mu\text{s}$	2566.1579 ₍₄₄₎	2578.331 ₍₉₅₎	2577.964 ₍₆₂₎	2574.1 _(6.9)	1256
$10^6 \varepsilon_{\tau 1} / \text{K}^{-1}$	128.360 ₍₆₀₎	128.21 ₍₈₀₎	128.06 ₍₅₃₎	128.21 ₍₁₄₎	130
$10^8 \varepsilon_{\tau 2} / \text{K}^{-2}$	4.981 ₍₃₄₎	4.97 ₍₃₄₎	4.78 ₍₂₃₎	4.91 ₍₁₁₎	6
$10^6 \alpha_V / 3 \text{K}^{-1}$	13.860 ₍₇₄₎	14.56 ₍₂₉₎	13.88 ₍₃₆₎	14.10 ₍₄₁₎	12
$10^5 \beta_V / \text{MPa}^{-1}$	1.81 ₍₂₅₎	2.56 ₍₄₁₎	1.87 ₍₅₂₎	2.11 ₍₄₀₎	3.3
$10^5 \beta_\tau / \text{MPa}^{-1}$	-0.471 ₍₁₄₎	-0.321 ₍₁₈₎	-0.371 ₍₂₃₎	-0.388 ₍₇₆₎	-0.95 to +1.2
$\frac{(\rho_{\text{VTD}} - \rho_{\text{EOS}})_{\text{r.m.s.}}}{\text{kg} \cdot \text{m}^{-3}}$	0.22	0.35	0.44		
$10^2 \frac{(\rho_{\text{VTD}} - \rho_{\text{EOS}})_{\text{r.m.s.}}}{\langle \rho_{\text{EOS}} \rangle}$	0.025	0.071	0.089		

Apparatus parameters for the three densimeters with a maximum pressure rating of 70 MPa, VTD-4, VTD-5, and VTD-6, were similarly determined by calibration by measuring their resonance period under vacuum and one or more reference fluids over a wide range of temperature and pressure. Of these three densimeters VTD-4 was calibrated most extensively, with vacuum, helium, toluene and water measurements each made at 9 temperatures between (283.15 and 473.15) K. For each of the three fluids over 125 measurements were made with pressure ranges of (1.01 and 65.01) MPa for helium, (1.01 and 65.07) MPa for water, and (1.02 and 65.08) MPa for toluene. The results of the regression of eq. (25) to the fluid densities calculated from the experimental pressure and temperature using the respective reference equations of state for each fluid^{22,23,25} are shown in Figure 4, with the best fit parameter values listed in Table 5.

The lower pressure rating of VTD-4 in comparison with VTDs-1 to 3 is reflected in the difference between the best-fit values of ρ_{00} , β_V and β_τ listed in Table 4 and Table 5. As the two types of vibrating tube have the same internal volume and radius²¹, the lower value of ρ_{00} reflects that the wall thickness of the densimeter with the lower pressure rating was 0.5 mm smaller than the densimeter with the higher pressure rating (see Table 2). The reduced wall thickness means that the magnitudes of both β_V and β_τ for VTD-4 are about three times as large as for VTD-1. Importantly, however, their ratio is the same for both VTD-1 and VTD-4, which were the two most extensively calibrated VTDs, with $\beta_V/\beta_\tau = -3.87 \pm 0.02$. The results obtained for VTD-2 and VTD-3 are also consistent with this ratio. If the regression of eq. (25) is re-done for VTDs-2 and -3 with the

constraint $\beta_V = -3.87 \beta_\tau$ imposed, the impact on the quality of the best fit is negligible even though there is one less parameter with the r.m.s. deviation increasing by only 0.01 kg m^{-3} .

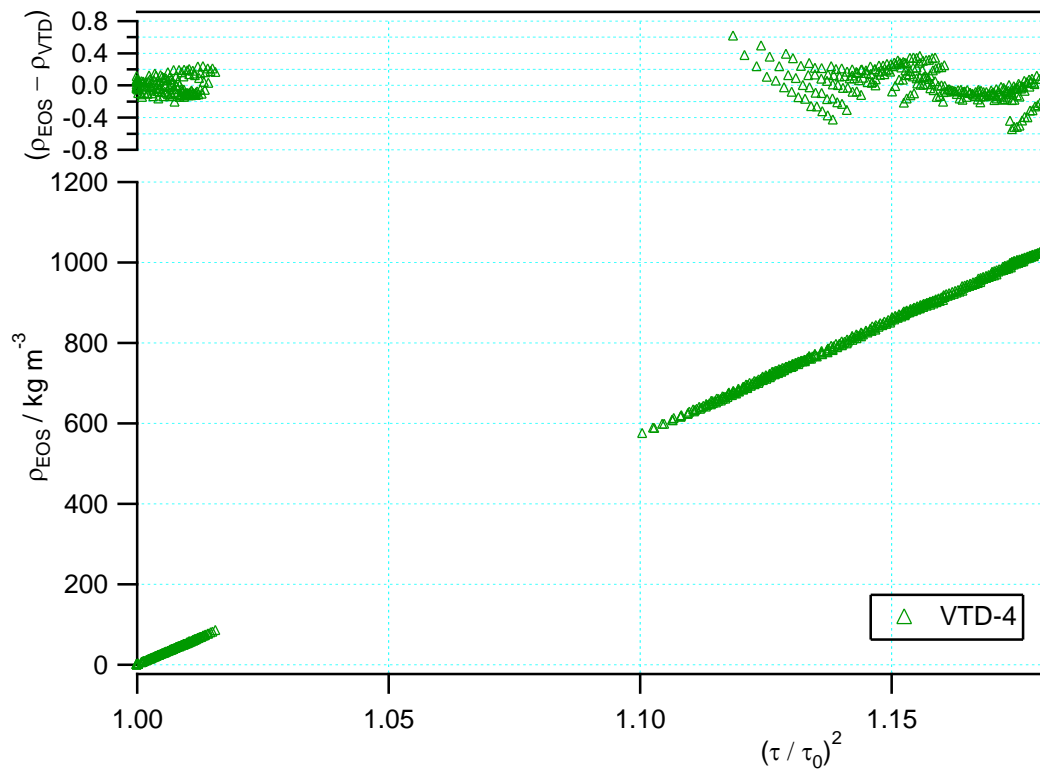


Figure 4. Lower panel: Water, toluene, and helium densities calculated using their respective reference equations of state^{22,23,25}, ρ_{EOS} , as a function of the squared normalised resonance period $(\tau/\tau_0)^2$ measured for VTD-4. Upper panel: Residuals between the EOS density and the density, ρ_{VTD} , calculated using eq. (25) with the parameters for VTD-4 listed in Table 5.

The 70 MPa rated densimeters VTD-5 and VTD-6 were used by Al-Ghafri et al.^{6,7} to measure the densities of twelve aqueous electrolyte solutions at molalities up to 6 mol kg^{-1} . While sufficient for that work, relative to the other VTDs studied here, the calibrations of VTD-5 and VTD-6 was the least extensive in terms of the number of reference fluids. The calibration measurements were conducted at temperatures (vacuum and water) and pressures (water) identical (within the uncertainty of the measurements) to those at which the aqueous solutions were measured. This approach ensures the mixture density measurements are reliable but the use of only one reference fluid means limits the information about β_V and β_τ that can be extracted from the calibration data. The vacuum measurements at nine temperatures between (283.15 and 472.96) K were sufficient to determine $\varepsilon_{\tau 1}$ and $\varepsilon_{\tau 2}$ by linear regression with statistical uncertainties equal to or smaller than any of the other densimeters. Determination of the other four parameters by non-linear regression of eq. (25) to the 71 water measurements made at the same temperatures at pressures between (1.10 and 68.60) MPa, gave values of β_V and β_τ that were not statistically significant, thereby confirming that the calibration data for VTD-5 and VTD-6 were inadequate for the purpose of completely resolving the pressure dependence of the apparatus. Accordingly, the regression of eq. (25) was re-done for VTD-5 and VTD-6 with the constraint $\beta_V = -3.87 \beta_\tau$, and the results are listed in Table 5. Imposing this constraint produced values of β_V that were statistically significant, and which were consistent with

the values both predicted and measured for the other VTDs rated to 70 MPa. Furthermore, the constrained regression had negligible impact on the quality of the fit achieved even though there was one less parameter, with the r.m.s. deviations increasing from those obtained with the over-parameterised fit by only 0.049 kg m^{-3} and 0.035 kg m^{-3} for VTD-5 and VTD-6, respectively.

Table 5. Best-fit values for the parameters in eq. (25) determined by calibration to vacuum and/or reference fluid data for VTD-4, -5, and -6, all of which were rated to 70 MPa. The absolute and relative r.m.s. errors of the best fits to each calibration data set are listed, as are the averages of each parameter across the three VTDs. The subscript numbers listed in parentheses correspond to the statistical uncertainty of either the best-fit value or the standard deviation of the averaged values. The (range of) value(s) of each parameter predicted using equations (11), (23) and (28)-(34) are listed for comparison. For VTD-5 and VTD-6, β_τ was not an adjustable parameter but was set by the constraint $\beta_V / \beta_\tau = -3.87$, which was the ratio found for VTD-1 and VTD-4.

Parameter	VTD-4	VTD-5	VTD-6	<VTD> ₄₋₆	PREDICTION
S_{00}	1.545481 ₍₄₆₎	1.627686 ₍₄₈₎	1.627544 ₍₃₉₎	1.600 ₍₄₇₎	
$\tau_{00} / \mu\text{s}$	2438.659 ₍₁₁₎	2389.1433 ₍₈₇₎	2389.219 ₍₁₃₎	2406 ₍₂₉₎	1508
$10^6 \varepsilon_{\tau 1} / \text{K}^{-1}$	127.81 ₍₁₁₎	128.135 ₍₈₅₎	128.11 ₍₁₃₎	128.03 ₍₂₀₎	130
$10^8 \varepsilon_{\tau 2} / \text{K}^{-2}$	4.830 ₍₅₁₎	4.712 ₍₄₀₎	4.731 ₍₆₁₎	4.758 ₍₆₃₎	6
$10^6 \alpha_V / 3 \text{K}^{-1}$	13.189 ₍₆₃₎	12.570 ₍₈₃₎	13.646 ₍₆₄₎	13.13 ₍₅₄₎	12
$10^5 \beta_V / \text{MPa}^{-1}$	5.365 ₍₈₀₎	5.140 ₍₂₅₎	5.017 ₍₁₉₎	5.14 ₍₁₃₎	5.7
$10^5 \beta_\tau / \text{MPa}^{-1}$	-1.382 ₍₀₇₎	-1.328	-1.296	-1.329 ₍₃₄₎	-5.2 to +2.7
$\frac{(\rho_{\text{VTD}} - \rho_{\text{EOS}})_{\text{r.m.s.}}}{\text{kg} \cdot \text{m}^{-3}}$	0.17	0.12	0.09		
$10^2 \frac{(\rho_{\text{VTD}} - \rho_{\text{EOS}})_{\text{r.m.s.}}}{\langle \rho_{\text{EOS}} \rangle}$	0.028	0.014	0.011		

Discussion and Conclusions

The consistency of the parameters values obtained from the calibration measurements across all six VTDs and with the values predicted from the thermoelastic and geometrical properties of the Hastelloy tube is striking, particularly considering that the predicted values are based on many assumptions, such as the homogeneity of the material used to form the tubes and the equivalence of straight and bent tubes. Across all six VTDs the temperature parameters $\varepsilon_{\tau 1}$, $\varepsilon_{\tau 2}$, and α_V have averages of $(128.12 \pm 0.18) \times 10^{-6} \text{ K}^{-1}$, $(4.83 \pm 0.12) \times 10^{-8} \text{ K}^{-2}$, and $(13.62 \pm 0.68) \times 10^{-6} \text{ K}^{-1}$, respectively, where the uncertainty bounds are the standard deviations and correspond to fractional values of 0.1 %, 2.4 % and 5.0 %. For the VTDs rated to 140 MPa, the fractional standard deviations of β_V and β_τ are both 20 %, which improves to 14 % for the values obtained via the constrained regression. For the VTDs rated to 70 MPa, the constrained regression produces values of β_V and β_τ which have fractional standard deviations of 2.5 %. Arguably, the most interesting finding is that the two most extensively calibrated densimeters, VTD-1 and VTD-4, which had quite different pressure

ratings and, thus, values of β_V nevertheless had identical ratios for the parameters β_V / β_τ . This observation enables the confident use of constrained regression to minimise the number of adjustable parameters in the apparatus model, further increasing its robustness. The similarity of the β_V / β_τ ratio possibly indicates that the mounting of the tube, and hence the effective constraint on the deformation of the tube's external radius is similar for the two types of VTD.

There are two primary advantages of using a robust model with physically-based adjustable parameters over other calibration approaches: the ability to extrapolate with reduced uncertainty, and a reduction in the number of calibration measurements required. The latter advantage was demonstrated in part for VTD-5 and VTD-6 where apparatus parameters consistent with those of VTD-4 could be obtained from only vacuum and water measurements using the constraint $\beta_V / \beta_\tau = -3.87$. To test the advantage relating to extrapolation, VTDs-1 to 4 were re-calibrated by excluding the water data and using the constraint $\beta_V / \beta_\tau = -3.87$. The results are shown in Table 6 and indicate that the increase in r.m.s. error when the extrapolated model is used to predict the measured water densities is less than 0.4 kg m^{-3} . This contribution to this increase in error of any non-linearity associated with the extrapolation to higher densities, as discussed by Kayukawa et al.¹⁶, is not considered, as no information about the VTD's counter mass was available.

The results presented here for six Hastelloy densimeters from Anton Paar indicate that these recently developed VTDs are well described by a physically robust model derived by extending the theoretical framework presented originally by Holcomb and Outcalt¹¹. It is quite possible that the design and manufacture of this particular class of VTDs means they are more stable and have apparatus parameter values closer to those predicted from the extended theoretical framework than would be the case for older models of VTD such as the DMA 512 and 512P. With any apparatus that requires calibration, it is important that the stability of that calibration over time be checked regularly and this remains the case for the Hastelloy VTDs discussed here. However, this work indicates that the number of calibration points as well as the frequency of calibration could be reduced relative to those required to previous apparatus models of the densimeter. In particular, for this class of VTD, the use of eq. (25) means that it should not be necessary to measure a reference fluid at every single (p,T) condition of interest.

Table 6. Changes in apparatus parameter values for VTDs-1 to -4 when the water data are excluded from the regression and $\beta_V / \beta_\tau = -3.87$ (NWC) relative to when the water data are included and both β_V & β_τ are free parameters (W) (see Table 4 and Table 5). The r.m.s. errors of the densities calculated with eq. (25) using the two sets of parameters, ρ_{VTD} , relative to those calculated with the reference equations of state for each fluid, ρ_{EOS} , are also listed. The r.m.s. error calculated for the NWC set of parameter values corresponds to an extrapolation of the model as it includes the measured water densities.

	VTD-1	VTD-2	VTD-3	VTD-4
$10^4 (S_{00}^{\text{(NWC)}} - S_{00}^{\text{(W)}})$	-0.006 ₍₂₆₎	0.51 ₍₁₅₎	0.87 ₍₁₆₎	-0.435 ₍₆₇₎
$(1/3)10^6 (\alpha_V^{\text{NWC}} - \alpha_V^{\text{W}})/\text{K}^{-1}$	-0.03 ₍₁₃₎	-1.76 ₍₇₃₎	-0.13 ₍₇₅₎	-0.38 ₍₁₀₎
$10^5 (\beta_V^{\text{NWC}} - \beta_V^{\text{W}})/\text{MPa}^{-1}$	0.00 ₍₂₅₎	1.50 ₍₄₂₎	0.70 ₍₅₂₎	-0.02 ₍₀₈₎
$10^5 (\beta_\tau^{\text{NWC}} - \beta_\tau^{\text{W}})/\text{MPa}^{-1}$		0.046 ₍₁₈₎	0.067 ₍₂₃₎	
$\frac{(\rho_{\text{VTD}} - \rho_{\text{EOS}})_{\text{r.m.s}}^{\text{NWC, extrap}}}{\text{kg} \cdot \text{m}^{-3}}$	0.22	0.72	0.84	0.20
$\frac{(\rho_{\text{VTD}} - \rho_{\text{EOS}})_{\text{r.m.s}}^{\text{W}}}{\text{kg} \cdot \text{m}^{-3}}$	0.22	0.35	0.44	0.17

The results presented in Table 4 and Table 5 show that six of the seven apparatus parameter values determined by calibration were consistent with predictions based on the theoretical framework and knowledge of the tube's material and geometric properties. The agreement of the five parameters that describe the variation of the VTD's resonance period with temperature and pressure with the predicted values is particularly significant. The ability to predict with reasonable precision the values of the apparatus parameters that should be obtained by calibration allows experimentalists to detect when inadvertent errors or problems affect their measurements with reference fluids. Such errors, which may arise for example from contamination of the reference fluid, poor temperature stability or uniformity, or changes in the calibration of their temperature or pressure transducers, can be difficult to detect in the absence of expected parameter values.

The two-step calibration process followed in this work also has advantages related to helping increase the confidence in the results of calibration measurements and/or helping to detect problems early. By obtaining the vacuum period data over the measured temperature range, the temperature dependence of the tube's spring constant can be determined directly by linear regression and compared with values estimated from the elastic properties of the tube material. This also reduces the number of parameters required during the non-linear regression of the high-pressure calibration data for reference fluids to four, or even three if a constraint is used to relate the pressure dependence of the tube volume and spring constant. Following this approach can help reduce parameter correlation and again improve the ability of experimentalists to detect unanticipated problems encountered during the calibration stage.

A further motivation for developing a robust model with physically-based parameters is to reduce the number of calibration measurements required, and potentially identify the minimum set of data required to reliably calibrate a VTD. Based on the results obtained here, the minimum data set for calibration includes either (a) vacuum plus two different reference fluids over the required (p, T) range if both β_V and β_T are treated as free parameters in the non-linear regression, or (b) vacuum plus one reference fluid over the required (p, T) range if the ratio β_V / β_T is constrained. For case (a), the purpose of measuring the second reference fluid is to enable the pressure dependence of the spring constant to be de-convolved from the pressure dependence of the tube volume. Accordingly it may be sufficient to only measure the second reference fluid to the extent necessary to enable reliable determination of β_T . For example, if the VTD is calibrated with water over the entire (p, T) range it may be sufficient to measure a gas such as helium or N_2 along only one or two isotherms to the highest pressure achievable, which is often set by the pressure of the gas cylinder. However, as demonstrated by the increased precision achieved in this work for VTD-1 and VTD-4 relative to the other densimeters, the wider the range of conditions and the more reference fluids that are included in the calibration data set the more precise the apparatus parameter determinations can be.

Finally, we conclude by considering the increase in uncertainty associated extrapolation of eq. (25) beyond the range of the calibration. When extrapolating to higher densities, the potential impact of non-linearity needs to be assessed and/or quantified. However, this is a systematic effect which can in principle be quantified, for example through the use of a reference fluid with an appreciable density difference to that of the calibrants, and therefore mitigated. Of the parameters listed in Table 1, it is the uncertainty of S_{00} that is most significant in terms of the resulting uncertainty of any extrapolation with density. Accordingly it is important that a reference fluid with as large a density as possible be used in the set of calibration measurements from which S_{00} is determined; for this reason deionised water should be included as a reference fluid whenever possible. The additional uncertainty associated with the extrapolated density calculated using eq. (25) will be approximately the uncertainty in ρ_M / S_{00} multiplied by the difference $\tau_{\text{ext}}^2 - \tau_{\text{max}}^2$, where τ_{ext}^2 is the resonance period measured for the extrapolated density and τ_{max}^2 is the resonance period corresponding to the maximum density measured during the calibration.

Extrapolation in either pressure or temperature is also improved using the robust model relative to other apparatus models, with the resulting uncertainty in the density at the extrapolated condition set by the uncertainty with which the apparatus parameters are determined during the calibration. Implicit in the derivation of eq. (25) was the assumption retention of the first and second order terms shown in the pressure and temperature expansions in eqs (13)-(16) was sufficient. The results presented here show that this is the case for the entire operating range of the VTDs considered here. Clearly, however, the uncertainty of the apparatus parameters depends on the range of the calibration data so it would always be best to ensure that reference fluid measurements span the desired temperature and pressure range even if they are made after the measurement of the unknown sample. Since any given temperature and pressure can be reached as readily with de-ionised water as arguably with any other fluid, there would appear to be little impediment to ensuring the calibration of the VTD with reference fluids covered the necessary (p, T) range, eliminating the need to extrapolate in pressure or temperature.

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