Solution to the pycnometer challenge

Olaf Rienitz · Axel Pramann · Carola Pape

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Solution

(1) The inner volume of the pycnometer, V_p , is readily obtained from the mass of pure water, m_w , it can hold (and the density of that water, ρ_w). The actual mass can be calculated from the air buoyancy correction factor K_w of the water (using the corresponding density of air, $\rho_{air1}=1.18073 \text{ kg m}^{-3}$), and the difference between the apparent masses of the filled and empty pycnometer (m'_{p+w} and m'_{p1} , respectively).

$$V_p = \frac{m_w}{\rho_w} = \frac{K_w \times (m'_{p+w} - m'_{p1})}{\rho_w}, \text{ where } K_w = \frac{1 - \rho_{air1}/\rho_{cal}}{1 - \rho_{air1}/\rho_w}$$

The density of the TMAH solution is determined in a similar way, using the volume of the pycnometer, V_p , and the apparent masses of the filled and empty pycnometer (m'_{p+s} and m'_{p2} , respectively), in addition to the buoyancy correction factor of the TMAH solution, K_s .

$$V_p = \frac{m_s}{\rho_s} = \frac{K_s \times (m'_{p+s} - m'_{p2})}{\rho_s}, \text{ where } K_s = \frac{1 - \rho_{air2}/\rho_{cal}}{1 - \rho_{air2}/\rho_s}$$

By combining these two expressions (thus eliminating V_p), we can obtain the conventional expression for the density of the TMAH solution, ρ_s :

$$\frac{K_w \times (m'_{p+w} - m'_{p1})}{\rho_w} = \frac{K_s \times (m'_{p+s} - m'_{p2})}{\rho_s}$$

$$\rho_s = \rho_w \frac{K_s \times (m'_{p+s} - m'_{p2})}{K_w \times (m'_{p+w} - m'_{p1})}$$

The buoyancy correction factor for the TMAH solution, K_s , is unknown at first, because the density of TMAH solution is still unknown. However, an estimated “starting” value of the density of the TMAH solution could be taken as $\rho_{s,0}=1000 \text{ kg m}^{-3}$. This yields the first estimate of the density, $\rho_{s,1}$ (note that $\rho_{air2}=1.17990 \text{ kg m}^{-3}$ is taken for the second experiment):

$$K_w = \frac{1 - 1.18073/8000}{1 - 1.18073/997.880} = 1.001 \ 0369$$

$$K_{s,0} = \frac{1 - 1.17990/8000}{1 - 1.17990/1000} = 1.001 \ 0336$$

$$\rho_{s,1} = 0.997 \ 880 \text{ g mL}^{-1} \times \frac{1.001 \ 0336 \times (15.1242 - 10.0348) \text{ g}}{1.001 \ 0369 \times (15.0216 - 10.0348) \text{ g}}$$

$$= 1.018 \ 41 \text{ g mL}^{-1}$$

Then, using this first estimate of ρ_s , an improved air buoyancy correction factor, $K_{s,1}$, is calculated. This, in turn, results a yet better estimate of the density, $\rho_{s,2}$.

$$K_{s,1} = \frac{1 - 1.17990/8000}{1 - 1.17990/1018.41} = 1.001 \ 0123$$

$$\rho_{s,1} = 0.997 \ 880 \text{ g mL}^{-1} \times \frac{1.001 \ 0123 \times (15.1242 - 10.0348) \text{ g}}{1.001 \ 0369 \times (15.0216 - 10.0348) \text{ g}}$$

$$= 1.018 \ 39 \text{ g mL}^{-1}$$

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O. Rienitz (✉) · A. Pramann · C. Pape
Physikalisch-Technische Bundesanstalt (PTB), Bundesallee 100,
38116 Braunschweig, Germany
e-mail: olaf.rienitz@ptb.de

Yet another iteration yields the density of TMAH, which is indistinguishable from the last iteration. Hence, we can state that the density of the TMAH solution is $\rho_s = 1.01839 \text{ g mL}^{-1}$.

(2) Neglecting the air buoyancy altogether yields a slightly different result that equals (within the number of digits) the result of the first iteration step, i.e., $\rho_s = 1.01841 \text{ g mL}^{-1}$.

(3) References [1] and [2] offer a much more elegant analytical solution which enables calculation of the density ρ_s in a single step. The weighing results of the empty and water-filled pycnometers can be written as follows:

$$m'_{p1} = m_p \frac{1}{K_p} = m_p \frac{1 - \rho_{\text{air}1} / \rho_p}{1 - \rho_{\text{air}1} / \rho_{\text{cal}}}$$

$$m'_{p+w} = m_p \frac{1}{K_p} + m_w \frac{1}{K_w} = m_p \frac{1 - \rho_{\text{air}1} / \rho_p}{1 - \rho_{\text{air}1} / \rho_{\text{cal}}} + m_w \frac{1 - \rho_{\text{air}1} / \rho_w}{1 - \rho_{\text{air}1} / \rho_{\text{cal}}}$$

Note that $m_w = \rho_w V_p$. By subtracting the above equations one can obtain the inner volume of the pycnometer, V_p :

$$V_p = \frac{m'_{p+w} - m'_{p1}}{\rho_w - \rho_{\text{air}1}} (1 - \rho_{\text{air}1} / \rho_{\text{cal}})$$

Likewise, weighing of the empty and sample-filled pycnometers can be described as follows:

$$m'_{p2} = m_p \frac{1 - \rho_{\text{air}2} / \rho_p}{1 - \rho_{\text{air}2} / \rho_{\text{cal}}}$$

$$m'_{p+s} = m_p \frac{1 - \rho_{\text{air}2} / \rho_p}{1 - \rho_{\text{air}2} / \rho_{\text{cal}}} + m_s \frac{1 - \rho_{\text{air}2} / \rho_s}{1 - \rho_{\text{air}2} / \rho_{\text{cal}}}$$

Again, note that $m_s = \rho_s V_p$. From the above equations one can obtain ρ_s :

$$m'_{p+s} - m'_{p2} = \rho_s V_p \frac{1 - \rho_{\text{air}2} / \rho_s}{1 - \rho_{\text{air}2} / \rho_{\text{cal}}}$$

$$\rho_s = \frac{m'_{p+s} - m'_{p2}}{V_p} (1 - \rho_{\text{air}2} / \rho_{\text{cal}}) + \rho_{\text{air}2}$$

Substitution of V_p yields the analytical solution to the pycnometer challenge:

$$\rho_s = \frac{m'_{p+s} - m'_{p2}}{m'_{p+w} - m'_{p1}} \times (\rho_w - \rho_{\text{air}1}) \times \frac{1 - \rho_{\text{air}2} / \rho_{\text{cal}}}{1 - \rho_{\text{air}1} / \rho_{\text{cal}}} + \rho_{\text{air}2}$$

This expression yields the density ρ_s in a single step which is not only more convenient but also enables straightforward estimation of the uncertainty.

$$\begin{aligned} \rho_s &= \frac{15.1242 - 10.0348}{15.0216 - 10.0348} \times (997.880 - 1.18073) \text{ kg m}^{-3} \\ &\times \frac{1 - 1.17990 / 8000}{1 - 1.18073 / 8000} + 1.17990 \text{ kg m}^{-3} \\ &= 1018.39 \text{ kg m}^{-3} = 1.01839 \text{ g mL}^{-1} \end{aligned}$$

This result is identical with that obtained from the iterative approach.

When sufficient amounts of sample solution are available, measurement of the density can be further simplified. The sample can be used to rinse the pycnometer directly after calibration with pure water. This eliminates the need for the drying of the pycnometer (and equilibration to room temperature). During such an experiment, the ambient conditions (air density) will not change significantly, resulting in $\rho_{\text{air}1} = \rho_{\text{air}2} = \rho_{\text{air}}$, $m'_{p1} = m'_{p2} = m'_p$, and a more elegant equation:

$$\rho_s = \frac{m'_{p+s} - m'_p}{m'_{p+w} - m'_p} \times (\rho_w - \rho_{\text{air}}) + \rho_{\text{air}}$$

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References

1. Spieweck F, Bettin H (1992) *Tech Mess* 59:285–292
2. Dieterle M (2011) http://ap.physik.unibas.ch/PDF/Manuals/English/Experiment_03.pdf

Further Reading

1. Rienitz O, Pramann A, Pape C (2013) *Anal Bioanal Chem* 405:5627–5628