Anal Bioanal Chem (2009) 395:7–8
DOI 10.1007/s00216-009-2937-z

ANALYTICAL CHALLENGE

# Solution to Mendeleyev vodka challenge

**Juris Meija**

Published online: 12 July 2009


Chemists have known for a long time that mixing alcohol with water results in a solution with a volume that is somewhat smaller than that of its constituents: mix equal volumes of water and ethanol and the resulting volume of the spirit will contract by some 4%. That is why no one speaks of the "conservation of volume", in contrast to the conservation of mass (forget relativity).

The strength of alcohol is a quantity frequently marred by local traditions. Before the proper analysis of organic compounds was established, a distilled spirit was "proved" by dissolving gunpowder in the spirit and trying to ignite it. If it would not burn, there was too much water. If it burned, the spirit was "proven"; hence the origin of the term "proof" [1, 2]. Alternatively, *prevue d'Hollande* of the French consisted of shaking the spirit in a phial, and observing the size, number, and bursting of the bubbles (beads): the larger and more numerous the beads, as well as the more quickly they break, the stronger the spirit [1]. From the mid-seventeenth century onwards, however, aerometers became the status quo in spirit analysis, owing to the large difference between the density of pure water and that of alcohol.

The related analytical challenge can be found at doi:10.1007/s00216-009-2710-3.

J. Meija (✉)
Institute for National Measurement Standards,
National Research Council Canada,
1200 Montreal Rd. M-12,
Ottawa, ON K1A 0R6, Canada
e-mail: juris.meija@nrc.ca

Nowadays the "alcoholic strength by volume" is legally defined as the ratio of the volume of ethanol, measured at 20 °C, contained in the mixture to the total volume of the mixture, measured at the same temperature [3]. This refers logically to the volume concentration and not the volume fraction [4]. The latter is the volume of a component divided by the total volume of the components *before* mixing. Although the truth be told, even simple terminology matters can sometimes be confusing. Much like the terms "accuracy" and "precision" are listed as synonyms in most dictionaries, so are sometimes the volume concentration, $\sigma$, and the volume fraction, $\phi$ (see, for example, the conflicting IUPAC definitions of the volume fraction [5, 6]).

Returning to Mendeleyev [7]; he found that the biggest volume contraction occurs when ethanol and water are mixed in the amount ratio of 1:3. Therefore, if anything, it would be this solution ($C_2H_5OH + 3H_2O$) that might be the candidate for the "perfect vodka". Consider 1 mol of $C_2H_5OH$ and 3 mol of $H_2O$. Such amounts correspond to 46.1 g of ethanol and 54.0 g of water. Hence, the mass fraction of alcohol in such a mixture is 46.1/(46.1+54.0) = 46%. From handbooks we gather that the density of such a solution (20 °C) is 0.923 g $L^{-1}$, whereas the densities of pure ethanol and pure water are 0.789 and 0.998 g $L^{-1}$, respectively [3]. Now, the alcoholic strength (volume concentration of ethanol) in such a solution is as follows:

$$\sigma_{\mathrm{EtOH}} = \frac{V_{\mathrm{EtOH}}}{V} = \frac{m_{\mathrm{EtOH}}\rho_{\mathrm{EtOH}}^{-1}}{m\rho^{-1}},$$

$$\sigma_{\mathrm{EtOH}} = \frac{46.1\ \mathrm{g} \times 0.789^{-1}\ \mathrm{L\ g^{-1}}}{100.1\ \mathrm{g} \times 0.923^{-1}\ \mathrm{L\ g^{-1}}} = 0.539.$$

Among vodkas of such strength is Japan's exquisite *Okuhida* rice vodka. Here's to alcohol: the cause of, and solution to, all of life's problems (Homer Simpson).

## References

1. Pereira J (1839) The elements of *materia medica*, part 1. Longman, London
2. Ashworth WJ (2001) Technol Cult 42:27
3. International Organization of Legal Metrology (1973) Recommendation no. 22: alcoholometry. International Organization of Legal Metrology, Paris
4. Dybkaer R (2007) Accred Qual Assur 12:661–663
5. Mills I et al (1993) Quantities, units and symbols in physical chemistry, 2nd edn. Blackwell, Oxford
6. Lehmann HP, Fuentes-Arderiu X, Bertello LF (1996) Pure Appl Chem 68:957–1000
7. Meija J (2009) Anal Bioanal Chem 394:9–10