Analytical Methods

Certification of the reference material of water content in water saturated 1-octanol by Karl Fischer coulometry, Karl Fischer volumetry and quantitative nuclear magnetic resonance

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ABSTRACT

Certified reference materials (CRMs) of water content are widely used in the calibration and validation of Karl Fischer coulometry and volumetry. In this study, the water content of the water saturated 1-octanol (WSO) CRM was certified by Karl Fischer coulometry, volumetry and quantitative nuclear magnetic resonance (Q NMR). The water content recovery by coulometry was 99.76% with a diaphragm-less electrode and Coulomat AG anolyte. The relative bias between the coulometry and volumetry results was 0.06%. In Q NMR, the water content of WSO is traceable to the International System (SI) of units through the purity of internal standard. The relative bias of water content in WSO between Q NMR and volumetry was 0.50%. The consistency of results for these three independent methods improves the accuracy of the certification of the RM. The certified water content of the WSO CRM was 4.76% with an expanded uncertainty of 0.09%.

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1. Introduction

Accurate measurement of water content is essential for determination of the purity of reference materials (RMs) and pharmaceuticals, and quality control of food products (Isengard, 2001; Rückold, Grobecker, & Isengard, 2001; Vogl & Ostermann, 2006; Yazgan, Bernreuther, Ulberth, & Isengard, 2006). Karl Fischer methods, including coulometry and volumetry, are widely used for water content measurements because of their specificity, precision, and convenience (Scholz, 1984). As an absolute method, the water content is determined by coulometry using the quantity of electricity consumed during the electrolysis according to Faraday's law (Scholz, 1984). The recovery of water by coulometry depends on the electrolytic efficiency, the proportion of side reactions that are affected by the composition of analytes and electrolytes (Andersson & Cedergren, 1987; Kato, Fujimoto, & Kakuda, 1992), and the structure of the electrode (with diaphragm or without diaphragm) (Cedergren & Jonsson, 1997, 2001; Margolis, 1997). Analyses of complicated matrices, such as food products, crude oils and transformer oils, are affected by the sampling methods which can include direct injection, oven evaporation, or azeotropic distillation (Kestens, Conneely, & Bernreuther, 2008; Margolis & Mele, 2001). Therefore, even for a simple substance like bioethanol, there was a large range for the water content when it was determined in an international comparison by national metrology institutes.

To increase the accuracy and consistency of results, water content RMs are employed in the calibration and validation of both volumetry and coulometry (Margolis & Levenson, 2000). The uncertainty in the water content of the RMs used in calibration should be taken into account in the uncertainty of the final results. The water content of water saturated 1-octanol (WSO) (standard reference material (SRM) 2890) has been certified by coulometry and volumetry by the National Institute of Standards and Technology (NIST). Because of its good accuracy and stability, SRM 2890 has been widely employed in calibration or validation. However, in the certification of SRM 2890, there is a relative bias of 1.3% for the water content between coulometry and volumetry, which is one of the main sources of the uncertainty. Furthermore, the two certified methods, coulometry and volumetry, are not completely independent in theory, which does not satisfy the requirements of RMs according to ISO Guide 34 (2000).

In recent years, quantitative nuclear magnetic resonance (Q NMR) has attracted attention as a new method for determination of the purity of organic substances (Pauli, Jaki, & Lankin, 2005). In Q NMR, the purity of analytes is traceable to the International System (SI) of units through the purity of the internal or external standard. Although there have been several reports on the measurement of the water content by Q NMR (Dais & Hatzakis, 2008), the application of Q NMR in certification of water content RMs remained an area to be explored. In the present study, Q NMR was used to certify the water content of WSO (referred to as WSO CRM) combining it with Karl Fischer coulometry and volumetry. The results obtained by the three methods were consistent

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after optimisation of coulometry and volumetry. The uncertainty budget of the WSO CRM is discussed.

2. Experimental

2.1. Materials

1-Octanal was purchased from Sinopharm Chemical Reagent Co. Ltd., (Beijing, China) and its purity was determined by the gas chromatography as 99.40% with a standard deviation (SD) of 0.01%. Reagents for Karl Fischer titration were purchased from Sigma–Aldrich Inc. (St. Louis, MO). Fully deuterated acetonitrile (acetonitrile-d) was purchased from Cambridge Isotopes Laboratories (Andover, MA). Ethylparaben certified RM (GBW(E) 100064) was produced by the National Institute of Metrology (Beijing, China).

To prepare WSO, 4 L of 1-octanol and 0.5 L distilled water were combined in a 5 L stoppered volumetric flask and vigorously mixed for 24 h using a magnetic stirrer with a Teflon-coated stir bar. The sample was left to sit for 3 days, and the WSO (upper layer) was decanted into a second stoppered volumetric flask and then dispensed into twenty-five 180 mL stoppered glass bottles. The WSO in the 180 mL bottles was dispensed in 5 mL aliquots into 10 mL dried ampoules and then the ampoules were flame sealed. Ampoules were randomly selected for coulometry ($n = 15$), volumetry ($n = 10$), and Q NMR ($n = 6$).

Two 20 mL crimp neck headspace vials with rubber septa (CNW Technologies GmbH, Düsseldorf, Germany) were dried at 95 °C for 24 h and then cooled to room temperature in a desiccator containing phosphorus pentoxide. The blank vial was filled with 10 mL pure 1-octanol and then sealed. The other vial was filled with 10 mL pure 1-octanol and weighed with a readability of 0.0001 g. Then, about 0.16 g distilled water was added and then sealed immediately. The mass of added distilled water was weighed with a readability of 0.0001 g. The water content of pure 1-octanol (approximately 0.015%) in the blank vial was determined by using coulometry. The water content of this standard was calculated based on the mass of the added water and the water content of the pure 1-octanol. The water content of the home-made water standard was about 2.0%. This water standard was employed in validation of coulometry and calibration of volumetry. It was prepared in the morning and used the same day.

2.2. Analytical methods

Coulometric measurements were performed by Karl Fischer titration with a DL 39 titrator (Mettler-Toledo Instrument Inc., Greifensee, Switzerland) using a cell with or without a diaphragm. In the titration with the diaphragm-cell, Hydranal Coulomat A, AG, AK and AG-H reagents were used as the anodic electrolyte, and Coulomat CG as the cathodic electrolyte. In the titration with the diaphragm-less cell, Hydranal Coulomat A, AG, AK, AG-H and AD reagents were used as the anodic electrolyte. There was 0.4 mg of water in each injection. The following conditions were used: electrolysis rate "normal"; polarisation current 2 μA; end voltage 100 mV; and minimum titration time 180 s. The drift was determined over 180 s.

Volumetric measurements were performed with a V30 volumetric Karl Fischer titrator (Mettler–Toledo). Two-component Karl Fischer reagents including Hydranal-Titrant and Hydranal-Solvent were used. The water equivalence was about 2 mg mL^{-1}. There was approximately 2 mg of water in each injection. The following conditions were used: polarisation current 4 μA; end voltage 100 mV; minimum titration time 195 s. The drift was determined over 300 s.

The Q NMR method is based on the directly proportional relationship between the signal response (integrated signal area, I_x) and the number of nuclei generating the corresponding resonance line, which is represented by Eq. (1) as follows:

$$x = \frac{I_x}{I_{Std}} \cdot \frac{N_{Std}}{N_x} \cdot \frac{M_x}{M_{Std}} \cdot \frac{m_{Std}}{m} \cdot P_{Std} \tag{1}$$

where x is water content of analyte; I_x and I_{Std} are the integrated signal areas of analyte and internal standard, respectively; N_{Std} and N_x are the spin numbers of the internal standard and analyte, respectively; M_x and M_{Std} are molar mass of water and internal standard, respectively; m_{Std} and m is the mass of analyte and internal standard, respectively; P_{Std} is the purity of internal standard.

The Q NMR measurements were performed with an Avance DRX-600 spectrometer (Bruker, Billerica, MA). Spectra were run with the following parameters: probe size, 5 mm; probe temperature, was 23.0 °C; excitation pulse angle, 45°; 32 K time domain points; 16 K spectral data points; pulse delay, 4.15 μs; relaxation delay, 32 s and number of scans, 32. The CRM of ethylparaben was used as the internal standard. The acetonitrile-d and the ethylparaben contained traces of water and the measured solution might absorb traces of moisture from the air. Consequently, a blank solution containing 10 mg of ethylparaben and the acetonitrile-d was prepared to determine the trace water content in these samples (Eq. (1)). A sample solution containing a 10 mg ethylparaben, 470 mg of WSO and the acetonitrile-d of the same mass was analysed by NMR. The total mass of water in the sample solution was determined using Eq. (1). The water of the blank solution was subtracted from the water of the sample solution and then the water content of the WSO was calculated.

The purity of the ethylparaben standard (P_{Std}) was determined by freezing point depression using the national purity standard and an equation derived from the van't Hoff equation (Eq. (2)) (Quinn, 1997). Ethylparaben (about 1 g) was heated until it melted, cooled until completely frozen, and then heated at a constant heat flow and melted slowly. The melting temperature was T_1 at time t_1 for melted fraction F_1 and T_2 at time t_2 for melted fraction F_2. When 1 mg of benzoic acid (99.995%, NIST 39J) was added to the analyte, the impurities amount-of-substance fraction increased from x to $(x + a)$. The melting temperature of this sample was T_1' at time t_1' for melted fraction F_1' and T_2' at time t_2' for melted fraction F_2'. If the results for these two experiments are the same ($t_1 = t_1'$ and $t_2 = t_2'$), then the melted fractions are equal ($F_1 = F_1'$ and $F_2 = F_2'$). The impurities amount-of-substance fraction (x) can be calculated using Eq. (2) as follows:

$$x = a \cdot \frac{T_2 - T_1}{(T_2' - T_1') - (T_2 - T_1)} \tag{2}$$

The result (x) was then subtracted from 100% to determine P_{Std}.

3. Results and discussion

3.1. Coulometry

The effects of the electrolyte, electrode structure and sample quantity on the coulometry were investigated using the home-made water standard (water content about 2.0%, expanded uncertainty (U) 0.007%, coverage factor (k) = 2). Fig. 1 shows the water recovery which is the ratio of the measured value to the prepared value, for coulometry with various Karl Fischer anolytes and electrodes with or without a diaphragm. The recoveries (standard deviation) for the diaphragm electrode using Coulomat A, AG, AK and AG-H were 98.44% (0.35%), 98.02% (0.31%), 97.84% (0.45%) and 98.57% (0.35%), respectively. The recoveries (standard deviation) for the electrode without diaphragm using Coulomat A, AG, AK,