Analytical Methods

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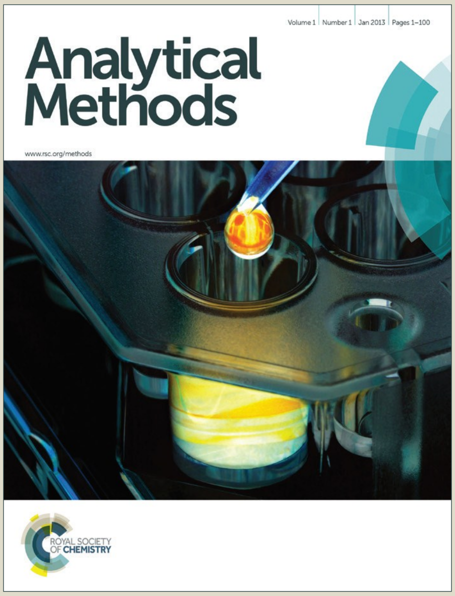

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ARTICLE

Certification of reference materials of sodium tartrate dihydrate and potassium citric monohydrate for water content

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Certified reference materials (CRMs) for water content in solid were used to calibrate Karl Fischer titrators or validate the measurement method for the accuracy and consistency of results. In present study, CRMs of sodium tartrate dihydrate and potassium citrate monohydrate for water content were investigated and certified. The stability of water content against humidity, the thermal stability and the composition of substances evaporated on drying of candidates of CRMs were characterized. The mass balance approach based on mass loss on drying was investigated to measure their water content. The Karl Fischer coulometry and volumetry were improved, especially in the sampling method, and utilized to certify two CRMs. Finally, the certified water content and its expanded uncertainty of two CRMs was 156.3 mg/g (1.3 mg/g, *k*=2) and 55.8 mg/g (0.6 mg/g, *k*=2), respectively.

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Introduction

Determination of water content with high accuracy is one of essential requirements for the analysis of food, pharmaceutical and chemical reagent.[1, 2] Karl Fischer titration, including Karl Fischer coulometry and volumetry, is selective, repeatable and accurate, and thus widely applied in the measurement of water content.[3]

The Karl Fischer volumetric titration is usually calibrated by the certified reference materials for water content.[4, 5] The Karl Fischer coulometry should be calibrated as well as the volumetry, because its water recovery varied by the electrode for electrolysis and the electrolyte.[6, 7]

Margolis *et al*. from National Institute of Standard and Technology (NIST) had developed SRM 2890 based on the water saturated octanol and certified it by both Karl Fischer coulometry and volumetry.[5] CRMs in liquid with water content ranging from 0.1 mg/g to 47.6 mg/g were developed by National Metrology Institute (NMI) of China (NIM) and Japan (NMIJ).[8-11] These CRMs for water content in liquid have been used in the calibration of titrator and the validation of method, which make the results more accurate and consistent.

However, the repeatability and reproducibility of water content in solid remain unsatisfactory, compared with those in liquid. In the international inter-lab trial, the relative standard deviation (RSD) of report value of water content of lactose monohydrate ranged from 1.1% to 2.1% corresponding to samples of different brands.[12] In the international comparison on purity of organic pure substances participating by NMIs, the means of water content of estradiol (CCQM K55.a), aldrin (CCQM K55.b), valine (CCQM K55.c) and digoxin (CCQM K55.f) is 5.02 mg/g, 1.57 mg/g, 0.85 mg/g and 1.2 mg/g with a RSD of 75%, 183%, 215% and 48%, respectively.[13] Besides of the inhomogeneity of analytes, the worse reproducibility might be partly due to the effect of moisture from environment or the carrier gas in the case of sampling by oven. Usually, the calibration or validation by reference materials for water content in solid is suggested to reduce the error by these effects.

Pure organic substances containing crystal water, such as sodium tartrate dihydrate, potassium citrate monohydrate and lactose monohydrate, are used as reference materials due to their stability of water content.[14, 15] It was reported that the water content of sodium tartrate dihydrate is stable in a wide range of humidity, and thus has a good stability during long storage.[14] Both Neuss *et al.* and Bryan *et al.* reported that the water content by Karl Fischer volumetry and that by the mass loss on drying are consistent with the theoretical water content (156.6 mg/g), and thus sodium tartrate dihydrate was regarded as a primary standard for water content.[14, 15] On the contrary, Beasley *et al*. reported that the water content of sodium tartrate dihydrate by Karl Fischer volumetry (160.1 mg/g) was more than that by mass loss on drying (156.4 mg/g), and the relative bias was about 2%.[16]

Though commercial reference materials of substances containing crystal water are available, there remains a need of CRMs for water content in solid certified by an accurate, traceable and universal method. The mass loss on drying is based on the hypothesis that the analyte has a good thermal stability, namely the major component and its impurities don't evaporate or decompose during drying at a high temperature. So the mass loss on drying is not applicable for substances prone to decompose at high temperature, such as lactose monohydrate. Even for sodium tartrate dihydrate, there is no evidence of composition analysis to demonstrate that the impurities of sodium tartrate dihydrate or the anhydrous product (sodium tartrate) do not evaporate or decompose on drying for a long time. So the accuracy and traceability of mass loss on drying might be questioned. On the other hand, Karl Fischer methods are selective for water, but their repeatability and accuracy for water content in solid remain to be improved for the certification of CRM.[16]

In present study, CRMs of sodium tartrate dihydrate and potassium citrate monohydrate for water content were developed. The stability against humidity, thermal stability and composition of evaporated substances on drying of candidates of CRMs were characterized. The mass balance approach based on the mass loss on drying, Karl Fischer coulometry and volumetry have been investigated to measure their water contents. Finally, the improved Karl Fischer methods were utilized to certify two CRMs.

Experimental

Materials

Four types of sodium tartrate dihydrate (CAS 6106-24-7) with analytical grade were purchased from Sigma-Aldrich Inc. (St. Louis, MO, USA) with the article number of 228729, S4797, V900100 and 34083. Potassium citrate monohydrate, 1-otanol (CAS 71-36-3) and all the reagents for Karl Fischer titration were also purchased from Sigma-Aldrich Inc. (St. Louis, MO, USA). The CRM of the water saturated octanol for water content (SRM 2890) was purchased from NIST (Gaithersburg, MD, USA).

Analytical methods

Water sorption isotherm (WSI) measurements were performed on Aqua Lab VSA (Decagon Inc., Pullman, WA, USA) with a chilled mirror hygrometer for the measurement of the water activity. The maximum water activity in WSI measurement is set as 0.85 aw. The flow rate of gas was 20 mL per min. The temperature of analyte was 25 ^{o}C.

Thermogravimetric (TG) measurements were performed on Pyris 1 thermogravimetric analyzer (TGA) (Perkin-Elmer Inc., Waltham, MA, USA) using a platinum pan. For the thermal stability test, 10 mg of sodium tartrate dihydrate or potassium citrate monohydrate was heated from room temperature to 300 ^{o}C with a rate of 10 ^{o}C per min. For the determination of water content, 10 mg of sodium tartrate dihydrate was heated to 150 ^{o}C with a rate of

10 ^{o}C per min and dried at 150 ^{o}C for 15 min. Potassium citrate monohydrate was heated to 200 ^{o}C and dried at 200 ^{o}C for 40 min.

Headspace gas chromatographic (HS-GC) measurements were performed on 6890 gas chromatography with a flame ionization detector (FID) and G1888 headspace sampling (Agilent Technologies Inc., Santa Clara, CA, USA). 10 mL vials were used. The mass of samples were 0.1 g. For sodium tartrate dihydrate, the temperature of oven, loop and transfer line of headspace was 150 ^{o}C, 160 ^{o}C and 160 ^{o}C, respectively. For potassium citrate monohydrate, that was 200 ^{o}C, 210 ^{o}C and 210 ^{o}C, respectively. The time for vial equilibrium was 15 min. The temperature of oven of chromatography was kept at 45 oC for 5 min and then increased to 230 oC at a rate of 10 oC per min. A column of DB-5MS with a length of 30 m, a film thickness of 0.25 µm and an inner diameter of 0.25 mm (Agilent Technologies Inc., Santa Clara, CA, USA) was used.

Headspace gas chromatography-mass spectrometric (HS-GC-MS) measurements were performed on Clarus 580 gas chromatography coupled with Clarus 8T mass spectrometry (Perkin-Elmer Inc., Waltham, MA, USA). 20 mL vials were used. The mass of sample, temperature of headspace sampling, time for vial equilibrium and temperature program of GC were same to that of HS-GC above. The mass spectrometric measurements were performed using a total ion flow model.

Karl Fischer coulometric measurements were performed by DL 39 Karl Fischer coulometric titrator (Mettler-Toledo Instrument Inc., Greifensee, Switzerland) using a diaphragmless electrode. Hydranal Coulomat AG was used as the electrolyte. The mass of sodium tartrate dihydrate and potassium citrate monohydrate were about 20 mg and 50 mg, respectively. The following conditions were used: electrolysis rate “normal”; polarization current 2 µA; end voltage 100 mV; extraction time 240 s; titration time 240 s. The drift was determined over 180 s.

Karl Fischer volumetric measurements were performed with a V30 Karl Fischer volumetric titrator (Mettler-Toledo Instrument Inc., Greifensee, Switzerland). Two-component Karl Fischer reagents including Hydranal-Titrant and Hydranal-Solvent were used. The water equivalence was about 2 mg mL^{-1}. The mass of sodium tartrate dihydrate and potassium citrate monohydrate was about 20 mg and 50 mg, respectively. The following conditions were used: polarization current 4 µA; end voltage 100 mV; extraction time 240 s; titration time 340 s. The drift was determined over 300 s.

Both Karl Fischer coulometric and volumetric titrator were placed in the glove box with a dew point from -76 ^{o}C to -80 ^{o}C indicating a volume proportion of water vapour from 0.5 ppm to 1 ppm. A MX5 electronic balance (Mettler-Toledo Instrument Inc., Greifensee, Switzerland) with a readability of 1 µg was used to weigh the mass of sample.

The mass balance approach based on the mass loss on drying was developed and used to determine the water content. The mass balance approach contains two steps. In the first step, about 0.5 g sodium tartrate dihydrate was dried in the oven box at 150 ^{o}C for 15 min, and the mass loss on drying was calculated. In the second step, the water content of residue of sample after drying was determined by the Karl Fischer coulometry in the glove box. The water content was calculated through the mass loss on drying and the water content of residue. In the determination of potassium citrate monohydrate by the mass balance approach, 0.5 g sample was dried in the oven box at 200 ^{o}C for 40 min and then the water content of residue was determined by Karl Fischer coulometry too.

Results and discussion

Water sorption isotherms

The water sorption isotherms of sodium tartrate dihydrate of four different article numbers were shown in Fig. 1 a, b, c and d. The initial water activity of four samples at 25 ^{o}C is 0.175, 0.154, 0.884 and 0.193 aw, respectively, which indicates that the water content of No. 228729, S4797 and 34083 is stable in a lower humidity ranging from 15.4 %rh to 19.3 %rh. The initial water activity of No. V900100 (0.884 aw) was more than the maximum of analytical method (0.85 aw), so the procedure was automatically finished and only one data point was recorded. It indicates that the water content of No. V900100 is stable in a high humidity of 88.4 %rh (Fig 1d), namely water of No. V900100 is prone to evaporate under the normal humidity of laboratory (30 %rh-60 %rh) and thus the water content decreases. Fig. 1 shows that the mass of analyte increased with the water activity. As the water activity increases from the initial value to 0.85 aw, the mass increase of No. 228729, S4797 and 34083 was 0.44%, 0.12% and 0.07%, respectively. For No. 228729, the mass increases obviously when the water activity is higher than 0.68 aw (Fig. 1a). Different stability of water content against humidity of sodium tartrate dihydrate might due to the synthesis process, especially the drying process. The results above indicate that the water content of No. 34083 has the best stability against the humidity, therefore No. 34083 was chosen as the candidate of CRM for water content. The mass of potassium citrate monohydrate increases obviously when the water activity is higher than 0.56 aw. As the water activity increases from the initial value to 0.85 aw, its mass increase was 3.6%, which indicates that potassium citrate monohydrate has a strong hygroscopicity at a high humidity. Neuss J. D. *et al.* investigated the water content stability of a series of compounds including sodium tartrate dihydrate and potassium citrate monohydrate under different humidity by using the static gravimetry.[14] Redman-Furey N. *et al.* investigated that by using the dynamic water vapor isotherms.[17] In present study, the water sorption isotherms of analytes from different article numbers were characterized, which is utilized for the screening of the candidate of CRMs and endows the development of CRM a convenience. For the stability of water content, the CRM of sodium tartrate dihydrate and potassium citrate monohydrate should be stored in the humidity ranged from 15%rh to 60%rh. The bottle of CRM should be sealed immediately after the sampling.

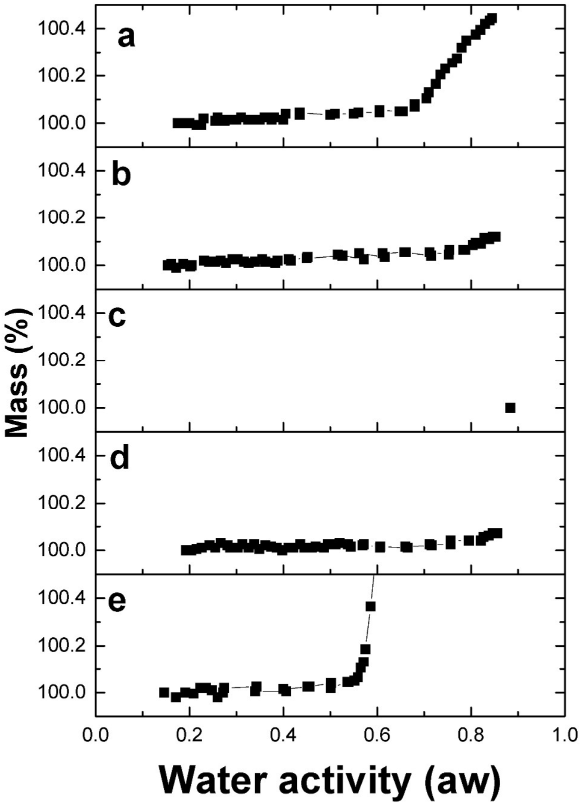

Fig 1. Water sorption isotherms of sodium tartrate dihydrate and potassium citrate monohydrate. (a, b, c and d is sodium tartrate dihydrate with the article number 228729, S4797, V900100 and 34083, respectively; e, potassium citrate monohydrate)

Thermogravimetry

Fig. 2 shows the mass vs temperature and the derived mass vs temperature curves of sodium tartrate dihydrate by TGA. As the temperature increased, the water of crystallization gradually evaporated from matrix, accompanying two peak of mass loss at 64 ^{o}C and 136 ^{o}C. It was explained that the two water molecules in one sodium tartrate dihydrate exists in different physical status, such as one in the capillary and one in the crystal.[17] The mass loss at 200 ^{o}C is 15.43%. There is no obvious mass loss for sodium tartrate over a temperature plateau from 160 ^{o}C to 250 ^{o}C, which demonstrates that sodium tartrate has a good thermal stability. On the contrary, the evaporation of the water in crystal from potassium citrate monohydrate is completed at the temperature higher than 250 ^{o}C, and then the decomposition of potassium citrate happens soon afterwards (Fig. 3). When the mass loss on drying at 250 ^{o}C is performed for the determination of water content of potassium citrate monohydrate, the decomposition might result in the overestimation of the water content.

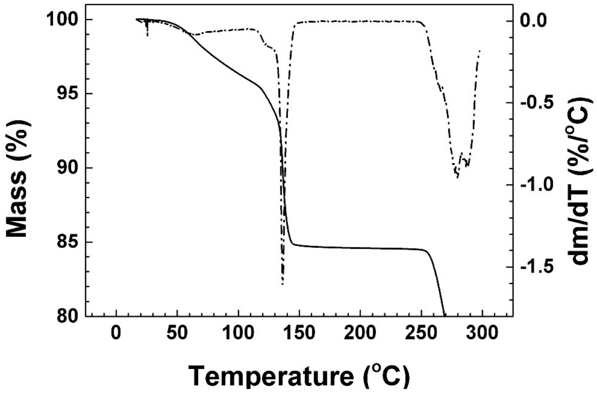

Fig. 2 The mass vs temperature and the derived mass vs temperature curves of sodium tartrate dihydrate.

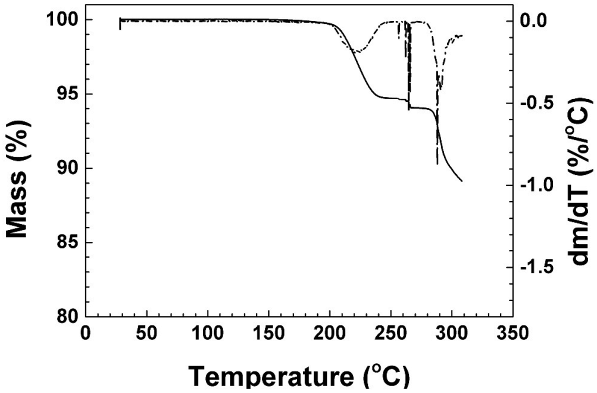

Fig. 3 The mass vs temperature and the derived mass vs temperature curves of of potassium citrate monohydrate.

Headspace gas chromatography and headspace gas chromatography-mass spectrometry

As shown in Fig. 4 and Fig. 5, HS-GC was utilized to analyze the products evaporated on drying of sodium tartrate dihydrate and potassium citrate monohydrate. The peaks at 3.60 min and 17.50 min appeared in both blank and analyte vial might be attributed to the product of the column bleeding or the decomposition of the rubber septum of vial (Fig. 4a and 4b). The peak at 4.54 min in analyte vial represents some decomposition product on drying at 150 ^{o}C, but it can't be identified through screening by the common volatile organic compounds (Fig. 4b). When the response factor of methanol was used instead of that of this unknown compound, its mass fraction in original sodium tartrate dihydrate is only 1.3 mg/kg. For potassium citrate monohydrate, since the drying temperature was 200 ^{o}C, more peaks appeared due to the decomposition of rubber septum (Fig 5a and 5b). The peak at 3.67 min and 4.27 min with low area might be attributed to the decomposition product of analyte.

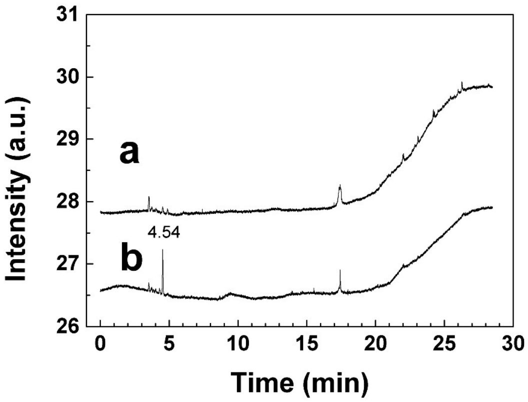

Fig. 4 HS-GC curves of sodium tartrate dihydrate. (a, blank vial; b, sodium tartrate dihydrate)

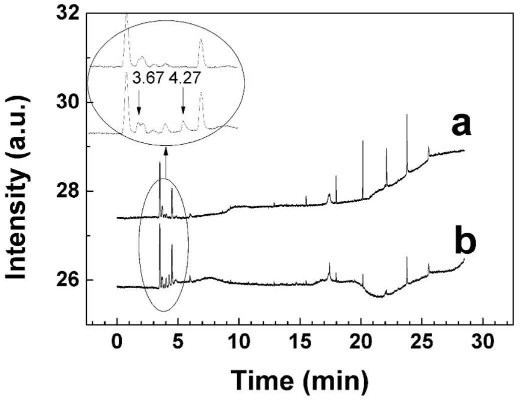

Fig. 5 HS-GC curves of potassium citrate monohydrate. (a, blank vial; b, potassium citrate monohydrate)

HS-GC-MS were also performed to analyze the evaporated product of sodium tartrate dihydrate and potassium citrate monohydrate. No obvious peak attributed to evaporated compounds appeared in the total ion chromatograms for both analytes. The water in crystallization of both compounds evaporates at a high temperature of 150 °C or 200 °C, which increases the inner pressure of headspace vial. Therefore, the mass of analyte for both HS-GC and HS-GC-MS was limited to 0.1 g to avoid the bursting of septum. The intensity of mass spectrometry was constricted by the low mass of analyte, which makes the identification of the evaporated product very difficult.

HS-GC and HS-GC-MS results indicated that the content of evaporated organic substances were very low. But HS-GC with FID can only detect the volatile organic compounds. If citrate acid, the precursor for the synthesis of potassium citrate monohydrate, existed in potassium citrate monohydrate as an impurity, it would decompose into carbon dioxide and water at the temperature above 175 °C which would escape from the detection by the HS-GC.

Mass balance approach

As seen in Table 1, the mass balance approach based on mass loss on drying was performed to determine the water content of sodium tartrate dihydrate and potassium citrate monohydrate. It was assumed that the total water is consisted by the water evaporated and the water in residue according to the mass balance theory, therefore the total water content of sodium tartrate dihydrate was the sum of that of two parts. The water content from mass loss on drying is 155.49 mg/g with a SD of 0.08 mg/g (Table 1). The water content of residue is 0.84 mg/g (on the basis of sodium tartrate dihydrate) with a SD of 0.06 mg/g (Table 1). So the total water content by the second approach is 156.33 mg/g. The traditional mass loss on drying for a long time was also performed. After a drying at 150 °C for 3 hours, the mass loss of sodium tartrate dihydrate was 156.02 mg/g with a SD of 0.07 mg/g (Table 1). The mass loss on drying by the thermogravimetry analyzer was also performed. The mass loss of sodium tartrate dihydrate was 153.63 mg/g with a SD of 0.42 mg/g (Table 1).

Table 1. Results of water content of sodium tartrate dihydrate and potassium citrate monohydrate by different methods.

No.	Method		Means (mg/g)	SD (mg/g)	*n*[a]
1[b]	Mass balance	Mass loss on drying	155.49	0.08	14
		Water content of residue	0.84	0.06	8
		Combination	156.33	/	/
	Mass loss on drying		156.02	0.07	8
	Thermogravimetry		153.63	0.42	45
	KF coulometry		156.22	0.22	18
	KF volumetry		156.34	0.32	15
2[c]	Mass balance	Mass loss on drying	54.27	1.33	11
		Water content of residue	3.38	2.21	11
		Combination	57.65	/	/
	Mass loss on drying		56.24	0.29	8
	Thermogravimetry		55.23	0.12	45
	KF coulometry		55.79	0.04	15
	KF volumetry		55.80	0.21	15

a, measurement times; b, sodium tartrate dihydrate; c, potassium citrate monohydrate.

Similarly, the water content by the mass balance approach of potassium citrate monohydrate was 57.65 mg/g (Table 1). Its water content by the traditional mass on drying is 56.24 mg/g with a SD of 0.29 mg/g (Table 1). Its water content by the thermogravimetry analyzer is 55.23 mg/g with a SD of 0.12 mg/g (Table 1).

The good repeatability of water content of sodium tartrate dihydrate by the mass balance approach is partly due to the large quantity of the sample mass (0.5 g) and the mass loss (0.078 g). Furthermore, drying for a long time is avoided in the mass balance method, which reduced the possibility of decomposition of analyte. So the mass balance approach should have a better accuracy in the theory. But, for potassium citrate monohydrate, the repeatability of results by the mass loss on drying for 40 mins (1.33 mg/g) and 3 hours (0.29 mg/g) are worse than that of sodium tartrate dihydrate (0.07 mg/g).

However, there are some disadvantages for the mass balance approach based on mass loss on drying. Firstly, impurity or anhydrous product of analyte might evaporate on drying even for short time, which would result the positive error of water content, especially for the substance with poor thermal stability. Secondly, the product after drying inevitably absorbs the moisture from environment during the cooling and weighing process, which results the negative error of water content. Finally, the repeatability of water content gets worse for the substance with lower water content. Therefore, the mass loss on drying is not a traceable, accurate and universal method for the certification of CRM for water content in solid.

Karl Fischer coulometry and volumetry

SRM 2890 was measured for the validation of methods. The result by the Karl Fischer coulometry was 47.6 mg/g with a SD of 0.2 mg/g. The results by the Karl Fischer volumetry was 47.7 mg/g with a SD of 0.2 mg/g. Both results were consistent with the certified value (47.3 mg/g, U=1.0 mg/g).[5]

The accuracy of water content in solid by Karl Fischer titration is used to be limited by the sampling method. According to our experiment, the SD and relative SD of water content of sodium tartrate dihydrate by the Karl Fischer coulometry with the direct addition at a humidity of about 20 rh% is 0.8 mg/g and 0.5%, respectively. When the solid analyte is added into directly, the moisture in the environment comes into the titration cell of Karl Fischer titrator during the opening of the cell and the addition of sample, and thus the drift becomes high and unrepeatable.[15] It was also demonstrated that the repeatability of results can not be improved by using an apparatus of oven by which the water in analyte is vaporized by heating and then transferred into Karl Fischer titrator cell for titration, the dissolution of analyte into anhydrous solvent or the addition of analyte under a pressure of carbon dioxide. Therefore, in the present study, the titrator was placed in a glove box where the atmosphere has an extreme low humidity. When the titration cell is open, the drift of titration remains 1 µg per min. The water content of sodium tartrate dihydrate determined by Karl Fischer coulometry in the glove box is 155.53 mg/g with a SD of 0.22 mg/g and the relative SD of 0.14% is even better than that of CRMs in liquid (0.24%).[9] The low and stable drift of Karl Fischer titration contributed to the repeatability of water content results.

We found that 20 mg sodium tartrate dihydrate releases water with a rate of 0.694 µg s^{-1} in the glove box. Redman-Furey *et al.* reported that sodium tartrate dihydrate releases water in a low humidity.[17] Therefore, the procedure of the sampling and weighing was improved as below. About 0.5 g sodium tartrate dihydrate was laid on the bottom of a glass weighing bottle with a diameter of 4 cm and a ground lid (Fig. 6a and 6b). 20 mg sample was added into a platinum crucible and weighed by the electronic balance, and then the crucible was placed above the 0.5 g sample layer in the weighing bottle (Fig. 6a). The sealed weighing bottle was transferred into the glove box and was opened, and then the sample was added into the titration cell. The process of the opening weighing bottle and the sample addition cost 20 s. The weighing bottle was then sealed and transferred outside the glove box (Fig 6b), and the empty crucible was weighed again, and thus the mass of added sample was calculated. Considering the analyte exposed in the glove box for 20 s, the mass of evaporated water is 13.9 µg. So the final water content of sodium tartrate dihydrate by the Karl Fischer coulometry is modified as 156.22 mg/g (Table 1).

Fig. 6 Schematic of weighing bottle, platinum crucible and sample. (a, sample in platinum crucible before sample addition; b, empty platinum crucible after sample addition)

A large quantity of raw material (0.5 g) laid on the bottom of the sealed weighing bottle produces a stable humidity equilibrated with the water activity of the analyte (20 mg), so the water content of analyte keeps stable during the storage in the weighing bottle whatever in the atmosphere or in the glove box. This modification endows the water content results of hydrophobic analyte titrated in extreme low humidity environment high repeatability and accuracy.

The mass of potassium citrate monohydrate is stable in the glove box, so there is no need to modify its water content due to water evaporation. Its water content by using Karl Fischer coulometry is 55.79 mg/g with a SD of 0.04 mg/g (Table 1).

The water contents of two candidates of CRMs by Karl Fischer volumetry are consistent with those by Karl Fischer coulometry (Table 1), which validates the accuracy of both Karl Fischer methods.

Both Karl Fischer methods were calibrated by the home-made water standard with a water content of about 20 mg/g and an expended relative uncertainty of 0.36%. This home-made standard was prepared by the gravimetry method and its water content traces to SI unit of mass of pure water.[9]

According to ISO guide 35, two or more methods based on different theory are combined to certify the reference materials.[18] SRM 2890 developed by NIST was certified by the Karl Fischer coulometry, volumetry and the interlaboratory studies based on coulometry.[5] CRMs of liquid for the water content developed by NIM and NMIJ were certified by the Karl Fischer coulometry and volumetry.[9-11] For the CRM of solid for the water content, the repeatability of results was limited by the sampling method. Since the glove box is unavailable for most laboratories, the interlaboratory studies produce a result with a poor repeatability and thus are not employed in the certification. As mentioned above, the mass balance approach is inappropriate for the certification due to the difficulty of the qualification and quantification of evaporated substance during drying. Therefore, the Karl Fischer coulometry and volumetry are combined to certify two CRM of solid for water content. And the means of results by two Karl Fischer methods was utilized as the certified value of water content.

The uncertainty of certified value was evaluated according to ISO guide 35.[18] The uncertainty of Karl Fischer method mainly comes from the dispersion of measurement results (type A uncertainty) and the factors besides of the statistic (type B uncertainty). One of the common attributions to the type B uncertainty is that from the home-made water standard (u_r, 0.18%).[9] The homogeneity tests of two CRMs were performed by using TGA. The uncertainty come from homogeneity is evaluated according to ISO guide 35.[18] The stability tests of two CRMs were performed by the Karl Fischer coulometry. The uncertainty come from stability is evaluated according to ISO guide 35, too. The expanded uncertainty (U) of two CRM was 1.3 mg/g and 0.6 mg/g with a coverage factor (k) of 2, respectively. The details of uncertainty budget are listed in the electronic supplemental material.

There are increasing needs of CRMs for water content in varied matrix, such as polymer, crude oil, liquid fuel, high pure organic solvent and electrolyte of li-ion battery, for the validation of methods in the routine measurements. Related investigation is on-going in our laboratory.

Conclusions

In this paper, the CRM of sodium tartrate dihydrate and potassium citrate monohydrate for water content were developed. The water sorption isotherms measurements were performed to characterize the stability of water content against humidity for the screening of the candidate for CRMs. The TGA, HS-GC and HS-GC-MS measurements results showed that sodium tartrate has a good thermal stability and the contents of evaporated substances of sodium tartrate dihydrate on drying are very low. The mass balance approach based on the mass loss on drying was developed to measure the water content of two candidates. Although the mass balance approach has a reduced systematic error resulted from the decomposition on drying, and a good repeatability in the case of sodium tartrate dihydrate, it is unsuitable for the certification of CRMs. The Karl Fischer coulometry and volumetry were improved, especially in the sampling, and utilized to certify the water content of CRM due to their accuracy, repeatability and universality. The certified water content and its uncertainty for sodium tartrate dihydrate was 156.3 mg/g and 1.3 mg/g (k=2). Those for potassium citrate monohydrate was 55.8 mg/g and 0.6 mg/g (k=2).

Acknowledgements

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