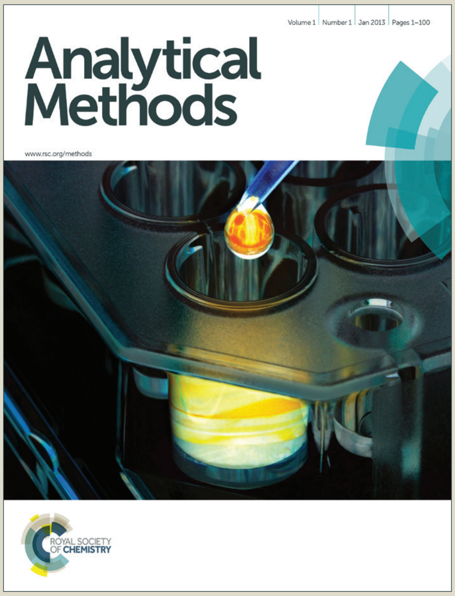
Analytical Methods



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-Technical Note-

Development of a Reliable Method to Determine Water Content by Headspace Gas Chromatography/Mass Spectrometry with Standard Addition Technique

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Abstract

A new and effective method for accurate water content determination using headspace gas chromatography/mass spectrometry (GC/MS) with the standard addition technique was developed. This method was applied to the analysis of commercially available water standards prepared in many kinds of solvent matrixes. The results obtained were consistent with the standard specifications and the values obtained by Karl Fisher (KF) titration within the range of uncertainty. Furthermore, the method was also applied to biofuel samples such as biodiesel derived from palm. Finally, the results revealed that headspace GC/MS is a superior technique for water content analysis, and the developed method is applicable to a variety of analytes for which KF titration is not appropriate.

Keywords: Water quantification, Water standards, Headspace gas chromatography/mass spectrometry (Headspace GC/MS), Standard addition method, Karl Fischer titration

Introduction

Precise determination of the water content in a variety of materials such as foods, pharmaceuticals, fuels, petroleum products, industrial materials, and chemical solvents is a very important issue. Therefore, development of simple, efficient, and reliable analytical methods for the quantification of water is imperative. Thus far, a number of analytical techniques such as monitoring thermally induced weight loss, Karl Fischer (KF) titration [1-5], the distillation method [5, 6], the hydride generation method [5, 7], gas chromatography (GC) [8-11], near infra-red spectroscopy (NIRS) [12], and quantitative nuclear magnetic resonance (qNMR) [13, 14] have been reported. However, only a few of these methods have been widely accepted and implemented. Even though quantification of water does not appear to be a difficult task, accurate results cannot be obtained without using methods that are appropriate for the analytes and for the measurement purpose. Furthermore, water absorption and desiccation of the analytes before and during the measurement are considerations that must be carefully addressed. Atmospheric moisture is one of the biggest sources of interference in the analysis of the water content of a sample; thus, water content analysis has a deceptive simplicity with unexpected complications.

Among the established techniques, monitoring thermally induced weight loss has the merits of being a simple and easily implemented procedure. A constant-temperature oven and a precision balance are the only instruments required to measure the change in the weight of an analyte after thermal treatment. However, the method is non-specific and often takes a long time. Volatile substances and thermal degradation products may be released from the analyte, and these may affect the measurement values. Therefore, the determination of water content is not as trivial an analysis as it may seem.

On the other hand, the KF titration (including coulometry and volumetry) is one of the most widely and frequently used techniques for the determination of water content. This method selectively detects water, in contrast with thermal weight loss analysis that detects the loss of any type of volatile substance. KF titration enables selective and precise determination of the water content within a short period, and has been adopted as a standard test method in many cases [5-7, 15-24]. Although KF titration is a well-established analytical method, there are some known disadvantages to this technique. KF titration is not necessarily a universal method since it is affected by interference from side reactions, atmospheric moisture, reagent instability, pH issues, and so on. In some cases, accurate results cannot be obtained when the analyte contain species that interfere with the KF reaction, such as oxidizing agents, reducing agents, aldehydes, ketones, free halogens, and most acids. For example, in the analysis of petroleum products containing sulfur, the presence of 1 mg kg^{-1} of mercaptan and 1 mg kg^{-1} of hydrogen sulfide led to respective errors equivalent of 0.3 and 0.6 mg kg^{-1} of the water content, compared with the value obtained by KF titration [5]. Therefore, analytical methods for the determination of the water content that utilize a principle different from that of the KF titration are highly desired.

Another approach that is widely used for the determination of the water content is based on gas chromatography (GC). GC is considered to be an effective tool, especially for analytes that are not appropriate for analysis by KF titration. The GC technique is not affected by interferences that affect KF reactions. The method enables separation of individual components, and water can be detected directly. In most previous studies, water was detected by means of a thermal conductivity detector (TCD) after separation by GC [8-11]. In recent years, a barrier discharge ionization detector (BID) [25] has also been used for the detection of water. These detectors respond not only to water but also to all compounds except the carrier gas; thus, the use of a mass spectrometer (MS) instead of TCD or BID should provide much more reliable data for the determination of water. However, the sample injection volume required for GC is quite small compared to that required for KF titration, which is another factor contributing to the extreme difficulty in preventing or controlling interference from atmospheric moisture in the sample and analytical system using conventional GC.

In comparison, headspace GC is a technique that relies on establishing an equilibrium between the species in an analyte and a gas phase in a sealed vial by heating for a specific period of time and analysing a sample of the gas phase by GC. This system offers the advantage of securing the injector and column against contamination; moreover, it is also possible to conduct a consistent and stable measurement of a number of samples with this system. Thus far, the technique has been applied to the analysis of flavour components in foodstuffs and chemical products, volatile organic compounds (VOCs) in environmental water, and so on [26]. However, to the best of our knowledge, only a few reports of the determination of water using headspace GC techniques are available. In principle, using headspace GC, atmospheric moisture being mixed into the analytical system would not occur [27-29].

In this study, we examine a headspace gas chromatography/mass spectrometry (GC/MS) method for direct and reliable determination of the water content of a sample using the standard addition technique. The efficiency of this approach is demonstrated with several liquid analytes.

Experimental

Reagents and chemicals

Propylene carbonate, 1-butanol, aniline, Aqualyte Water Standard 1, Aqualyte

Water Standard 10, and molecular sieve 3A 1/16 were purchased from Kanto Chemical (Tokyo, Japan). Benzaldehyde, Hydranal-Coulomat AG-H, Hydranal-Coulomat CG, and Hydranal-Water Standard 1 were obtained from Sigma-Aldrich Japan (Tokyo, Japan). Cyclohexanone was purchased from Wako Pure Chemical Industries (Osaka, Japan). Aquamicron Water Standard 0.2 mg, Aquamicron Water Standard 1 mg, and Aquamicron Check Solution P were obtained from Mitsubishi Chemical Corporation (Tokyo, Japan). KEMAQUA Water Standard 10 was purchased from Kyoto Electronics Manufacturing (Kyoto, Japan). NMIJ CRM 4222-a (Water in mesitylene (0.1 mg g^{-1})) was obtained from the National Metrology Institute of Japan (NMIJ, Tokyo, Japan). The water used in this study was purified with a Milli-Q Integral 3 (Millipore, Billerica, MA, USA) system.

Headspace GC/MS

Headspace sampling was performed by using a Turbo Matrix 40 (PerkinElmer, Waltham, MA, USA) instrument. A GCMS-QP2010 Plus (Shimadzu, Kyoto, Japan) gas chromatograph was utilized. The water was separated by using a DB-WAX column (60 m × 0.3 mm i.d., 0.5 μm film thickness; Agilent Technologies, Palo Alto, CA, USA). The conditions of the headspace sampler and GC/MS are summarized in Table 1. The equilibration temperature was set to 50 °C and the temperature of the transfer line and needle was set to 55 °C.

Standard addition method

To minimize contamination from atmospheric moisture, all samples and standard solutions were handled in a glove box under dry nitrogen (dew point: ca. -20 °C; purged with ca. 2 L min^{-1} nitrogen gas). All glassware items used in this study were heated at

150 °C in an oven for about 1 h and then cooled back to room temperature in a desiccator.

Quantification of water was carried out by using 1-butanol as an internal standard (IS) using the standard addition method [26, 30]. 1-Butanol was dehydrated over molecular sieves for a few days in advance. The series of the water standard solutions were prepared in a glove box by gravimetric mixing with water and 1-butanol. The prepared standard solutions were immediately added to the 6 mL of the samples in 22 mL headspace glass vials and were sealed with perforated aluminium caps fitted with butyl rubber septa (PerkinElmer). After sealing, the vials were removed from the glove box and were analysed by headspace GC/MS.

Coulometric KF titration

The coulometric KF titration was performed by using an MKC-510N (Kyoto Electronics Manufacturing, Kyoto, Japan) instrument with a diaphragm cell. Hydranal-Coulomat AG-H and CG were used as the anolyte and catholyte solutions, respectively. The wait time for titration was set at 0 s, and the titration period was 300 s. A 5 mL gas-tight syringe was used for sampling and was weighed using a precision balance (AB204; Mettler Toledo, Greifensee, Switzerland) calibrated by the Japan Calibration Service System (JCSS). The water content obtained by coulometric KF titration was calculated as described in our previous reports [31, 32].

Results and Discussion

Optimization of the conditions for headspace GC/MS and analysis of water content in propylene carbonate

Firstly, propylene carbonate was used to optimize of the water content determination by headspace GC/MS technique. Propylene carbonate is one of the most widely used organic solvents for commercially available water standards. The model analytes were prepared by performing gravimetric mixing with dehydrated propylene carbonate and pure water in the glove box; the water contents were ca. 0.5, 1, and 2 mg g^{-1}. They were stored in the glass vessels with mininert valves in the glove box. The water contents measured by KF titration were almost the same as the calculated values determined via gravimetric mixing and did not changed during preservation.

The water was separated by using a polyethylene glycol stationary phase column (DB-WAX) and the water peak was characterized by good efficiency and symmetry. Water was measured at *m/z* 18 and IS at *m/z* 56. The conditions of the headspace sampler were examined in detail. Using propylene carbonate as a matrix solvent, good reproducibility was obtained when the equilibration temperature was set to 50 °C and the equilibration time was set to 15 min. Because this method does not require heating of the analytes to high temperature, it should also be applicable to thermal sensitive samples. In addition, the areas of the water peaks showed good linearity over a wide range varying from 0.25 to 50 mg g^{-1} (correlation coefficient: $r^2 = 0.9995$).

Figure 1 shows typical mass chromatograms for the analysis of water in propylene carbonate using 1-butanol as an internal standard. Quantification of the water content was possible with the standard addition method, and the calibration curves showed good linearity with a high correlation coefficient ($r^2 > 0.993$). To validate the water determinations, the results of the headspace GC/MS analysis were compared with those obtained from coulometric KF titrations. The values obtained via headspace GC/MS were almost the same as those obtained using KF titration.

Figure 2 shows a comparison of the results from headspace GC/MS and KF titration analyses of water in propylene carbonate. The results were significantly consistent. To validate the headspace GC/MS method, the samples were analysed three times at each concentration and the obtained values were compared to those obtained by KF titration. Even though the water contents obtained by the headspace GC/MS method tend to be higher than those obtained by KF titration, the differences were within 4.7 %.

Analysis of water standards using headspace GC/MS method

The developed headspace GC/MS method was applied to the analysis of a variety of commercially available water standards. The water contents obtained by the developed method were compared with the manufacturer guaranteed values and with those obtained by KF titration. Table 2 summarizes the water contents determined for the commercially available water standards obtained by coulometric KF titration and headspace GC/MS. Even though a variety of organic solvents were used for these water standards, the water contents obtained by the headspace GC/MS method were consistent with the guaranteed values and the values obtained by KF titration. Therefore, the validity of the headspace GC/MS method was confirmed. By using the method, accurate determination of water content in water standards that contain many kinds of solvent matrices was accomplished. The developed method is highly sensitive and is also applicable to analytes that contain interferences that preclude the use of the KF titration.

Analysis of water contents of biodiesel fuels and analytes not appropriate for KF titration using headspace GC/MS method

The developed method was applied to the analysis of biodiesel fuels derived from palm. Precise analysis of the water content of biodiesel fuels is significant since water in fuel is subject to regulation and the water content of biodiesel fuels has been regulated to less than 0.5 mg g^{-1} in many countries. In this case, 1-butanol played the role of a solubilizing agent as well as an internal standard. The water contents obtained by the headspace GC/MS method and KF titration were 0.430 and 0.421 mg g^{-1}, respectively, which were within the experimental error.

One of the main advantages of using headspace GC/MS is that the method is applicable to analytes that are not appropriate for KF titration, such as those containing interfering substances. Table 3 shows the results of headspace GC/MS analysis of such analytes. Aniline, which is an electrode response compound, benzaldehyde and cyclohexanone (which are carbonyl compounds), canola oil that contains an antioxidant agent, etc., were successfully analysed. The developed method is thus applicable to analytes containing interferences that preclude the application of KF titration.

In summary, the developed method is expected to utilize in many areas as an alternative technique for the determination of water content that is completely different in principle from KF titration.

Conclusions

In this study, a new analytical method for the determination of the water content using headspace GC/MS with the standard addition method was successfully developed. By using this method, accurate determination of water in commercially available water standards and certified reference materials that contain a variety of organic solvent matrixes was accomplished. The obtained results were consistent with the guaranteed values and the values obtained using the conventional KF titration within the range of uncertainty. Furthermore, the method was also applicable to biofuel samples such as biodiesel derived from palm. The results revealed that headspace GC/MS, for this specific case, is superior to the KF titration for water content analysis. The developed method is applicable to a variety of analytes that contain interferences which make them unsuitable for KF titration. The newly developed headspace GC/MS method is expected to find applicability in many fields as a new technique for the determination of water that is completely different in principle from KF titration.

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Table 1 Conditions of headspace GC/MS

Headspace sampler parameters	
Sample temperature	50 °C
Transfer line temperature	55 °C
Needle temperature	55 °C
Equilibration time	15 min
Pressurization time	2 min
Withdrawal time	0.2 min
Injection volume	0.02 mL
GC/MS parameters	
Carrier gas	Helium
Carrier flow rate	1.11 mL min^{-1} (40 kPa)
Split ratio	400:1
Oven profile	50 °C for 5 min
	50–200 °C at 10 °C min^{-1}
	200 °C for 2 min
Inlet temperature	150 °C
Ion source temperature	200 °C
Interface temperature	200 °C
Scan	*m/z* 50–250

Table 2 Comparison of water contents of water standards determined by KF titration and headspace GC/MS method.

Name	Solvent	Guaranteed value (mg g^{-1})	Water content (mg g^{-1})	
			KF titration	Headspace GC/MS
Aqualyte Water Standard 1	Anisole/Diglyme	1.000	0.993	0.986
Aqualyte Water Standard 10	Diglyme	10.00	9.98	10.0
Aquamicron Water Standard 0.2 mg	Propylene carbonate	0.203	0.201	0.224
Aquamicron Water Standard 0.2 mg	1-Octanol$^{1)}$	0.200	0.191	0.188
Aquamicron Water Standard 1.0 mg	Propylene carbonate	0.999	0.997	1.02
Aquamicron Check solution P	Propylene carbonate	3.2–3.5	3.39	3.42
Hydranal-Water Standard 1.0	Anisole/Propylene carbonate	1.000	1.01	1.03
KEMAQUA Water Standard 10	Propylene carbonate	9.90	9.78	9.67
NMIJ CRM 4222-a (Water in mesitylene)	Mesitylene	0.134$^{2)}$	0.133	0.136

1) Previous lot

2) Certified value (mg g^{-1})

Table 3 Water contents of analytes that contain substances that interfere with KF titration, determined by headspace GC/MS method.

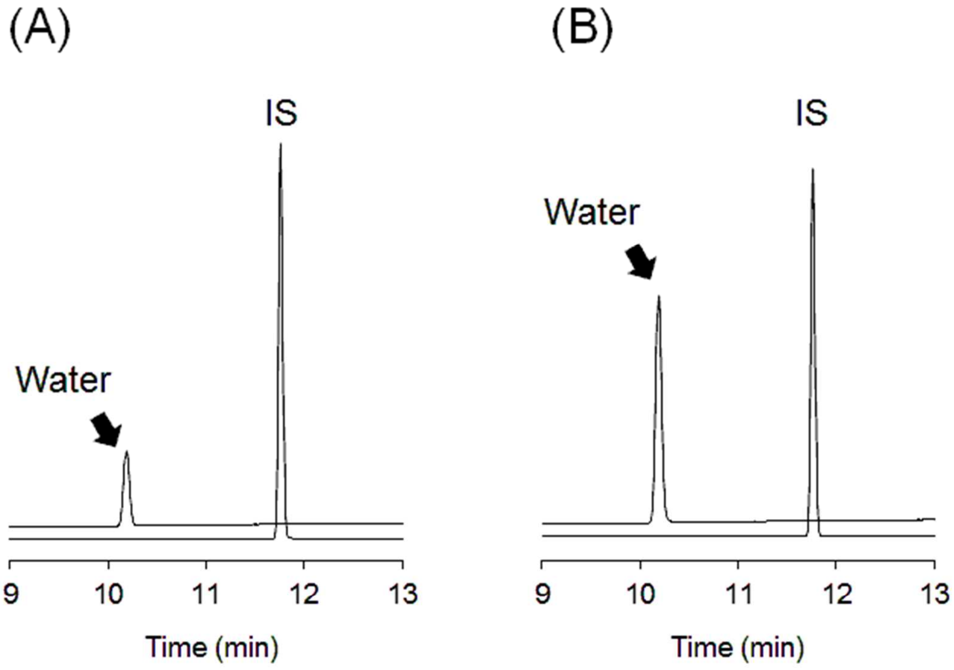
Analyte	Water content (mg g^{-1})
Aniline	0.288
Benzaldehyde	2.730
Cyclohexanone	0.547
Canola oil (containing antioxidant agent)	0.928

Figure Captions

Fig. 1 Typical mass chromatograms of water in propylene carbonate (A) without and (B) with addition of water (equivalent to 1.1 mg g^{-1} water).

Water was measured at *m/z* 18 and IS at *m/z* 56.

Fig. 2 Comparison of results from headspace GC/MS and KF titration for the determination of water in propylene carbonate.



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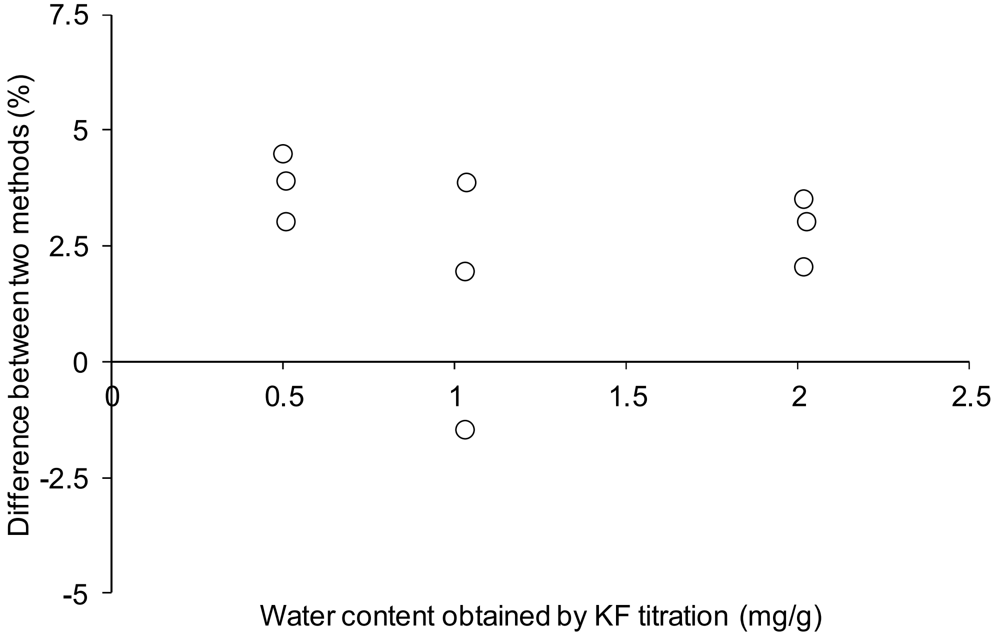

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