

Screening of water content in organic solvents using headspace gas chromatography flame ionization detector following calcium carbide reaction

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ABSTRACT

A simple method has been developed for the indirect determination of the trace water content in various organic solvents using reaction of water with calcium carbide to convert to acetylene. The sample and calcium carbide are placed in a closed sampling vessel, heated using a known temperature profile, and the acetylene in the vessel is sampled for analysis. Gas-tight syringe headspace-gas chromatography is used for determination of acetylene. Optimum extraction conditions have been evaluated with respect to temperature, calcium carbide, and stirring rate. In our experiments, good linearity ($r^2 = 0.9947$) and precision (R.S.D. < 10%, $n = 3$) were achieved. The limit of detection (LOD) and the limit of quantification (LOQ) were 54 and 181 mg L⁻¹, respectively. This technique is a promising pre-treatment method for the simple, rapid, accurate and precise analysis of water content in organic solvents. © 2014 Trade Science Inc. - INDIA

KEYWORDS

Headspace;
Water;
Acetylene;
GC/FID;
Organic solvent.

INTRODUCTION

The water content in organic solvents is often able to obviously affect the reactions of organic compounds, and it even makes a decisive influence on the productions, yield and selectivity of the reactions. In modern synthetic chemistry, significant effort may be expended to exclude moisture from reactions. In medicines, chemical products, foods and synthetic fibers, water content is one of the important characteristic data. Analytical testing for the presence and concentration of water is one of the most frequent, important, and ubiquitous measurements made in modern industrial society. Thus, a versatile, simple, and efficient analytical technique for

the accurate quantification of water is imperative. Therefore, determining water content in organic solvents is not only often encountered but also an important problem. Water content often has a great importance on organic reactions, and even decides the reaction products, yield or selectivity. The Karl Fischer^[1], gas chromatography^[2], fluorine nuclear magnetic resonance spectroscopy (F-NMR) spectroscopy^[3] and spectroscopic method^[4,5] are often employed in determining water content. But the methods have disadvantages such as low reaction velocity, being easily disturbed, bad precision, low sensitivity, time consuming, high cost or toxicity.

Existing physical and chemical methods for quan-

titative measurement of water in organic solvents are not well suited for rapid trace water analysis at the scale (1 mL total solvent volume). Sample preparation is a necessary part of any analytical procedure. Headspace gas chromatography is the analysis of the volatile and semi-volatile organic compounds in the gas headspace above a sample in a chromatography vial. 0.1-10 grams or milliliters is the typical sample size for headspace analysis, and virtually any sample that's not highly volatile can be tested. In static headspace analysis, a liquid or solid sample is placed in a vial, sealed and heated to a specific temperature so that the volatile components escape into the headspace above the sample. The headspace gas is then injected into a gas chromatograph which separates the various components of the sample based on size and polarity. Static headspace analysis is ideal for analyzing volatile compounds such as residual solvents or low molecular weight additives. Developing versatile, rapid, and accurate analytical techniques for the detection and quantification of water in a variety of materials remains an important and ubiquitous analytical problem. Derivatization is another technique that can be used to increase sensitivity and chromatographic performance for specific compounds. This paper suggests the use of indirect detection (that is, reacting water with calcium carbide to convert to acetylene) of water content of organic solvents and static headspace determination of produced acetylene by gas chromatography flame ionization detector.

MATERIALS AND METHODS

Reagents

Benzene, cyclohexan, isooctane, heptanes, ethyl methyl ketone, propanol, methanol, 1-butanol, amyl alcohol, toluene and para-xylene were purchased from Merck. All the solvents and reagents were analytical grade. Toluene was used as internal standard. Technical grade Calcium carbide (~80%) prepared from Sigma-Aldrich Company. Water was purified by a Direct-Q 3 UV with a pump system (Millipore, Molsheim, France). Stock solutions containing 10000.0 mg L⁻¹ of water was prepared in dried para-xylene. The working solutions were prepared in para-xylene daily by ap-

propriate dilution of the stock solution.

Apparatus

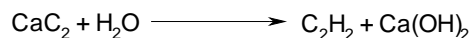
A DANI GC system with split-splitless injection port was used in all experiments. The GC system was equipped with an flame ionization detector. The fused silica CP wax 52 column used was 50 m length, 0.32 mm diameter with 0.2 μm film thickness. The injector port was operated with split ratio of 15 and temperature was kept at 250 °C, while the detector temperature was maintained at 300 °C. The column oven temperature was 100 °C. High purity nitrogen was used as carrier gas (1.0 mL min⁻¹) and make-up gas (30 mL min⁻¹). Hydrogen and air were used as detector gases at 30 mL min⁻¹ and 400 mL min⁻¹, respectively. A 100.0 μL gas tight microsyringe with a bevel needle tip was used for the injection.

Sample preparation method

A 6.0 mL portion of the sample solution, 0.5 mL of toluene (internal standard) and 0.07 g calcium carbide were transferred into a 10-mL glass vial with a PTFE-silicon septum (Supelco) containing a 12 mm × 1.5 mm magnetic stirring bar. The sample vial was maintained at a constant temperature using a water bath. Once the ample has reached equilibrium, the 100.0 μL aliquot is taken from the headspace using the gas-tight syringe, and was injected into the GC.

RESULTS AND DISCUSSIONS

When calcium carbide comes into contact with water, a chemical reaction immediately begins, which yields two new compounds, one of which is acetylene.



According to Henry's law the solubility of a gas in a liquid is directly proportional to the partial pressure of the gas above the liquid. Henry's law can be put into mathematical terms (at constant temperature) as

$$p = k_H c$$

where p is the partial pressure of the solute in the gas above the solution, c is the concentration of the solute and k_H is a constant with the dimensions of pressure divided by concentration. The constant, known as the Henry's law constant, depends on the solute, the solvent and the temperature.

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The rate at which acetylene partition out of the sample matrix and into the headspace, as well as the equilibrium concentration of acetylene in the headspace depends on several parameters. Temperature, amount of calcium carbide, and mixing can be used to improve the transfer of acetylene from the sample into the headspace of the vial.

Effect of temperature

Extraction temperature should be optimized first since it plays the most important role in the extraction process by controlling the diffusion rate of analytes into the headspace. The temperature of equilibration had a dramatic effect on the FID response for acetylene. The effect of temperature was studied in the range of 28-48°C, and the results are shown in Figure 1. Increasing the temperature till 39°C improved peak area of acetylene. Because solubility of permanent gases usually decreases with increasing temperature at around the room temperature, the partial pressure a given gas concentration has in liquid must increase. At higher temperatures, according to Henry's constant, the pressure of vial was increased and, consequently the septum was damaged. Thus, the optimum extraction efficiency was achieved at 39°C and this temperature was selected for the subsequent experiments.

Amount of calcium carbide

The effect of amount of calcium carbide in the range of 0.03 to 0.07 g was studied. An increase in calcium carbide produces an increase in acetylene peak area

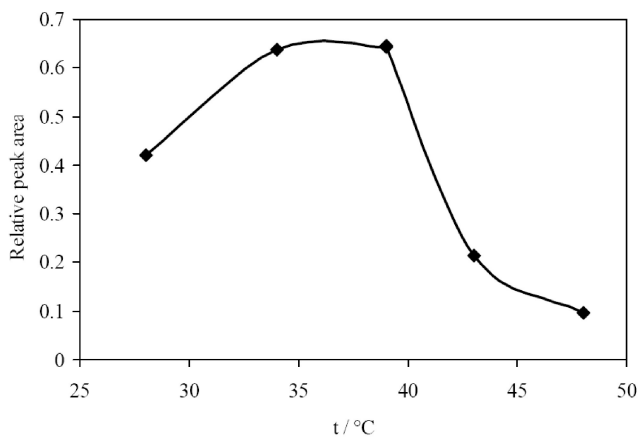


Figure 1 : Effect of temperature on headspace extraction of acetylene. conditions: volume of sample: 7.0 mL, volume of toluene (internal standard): 0.50 mL, amount of calcium carbide: 0.05 g, stirring rate: 300 RPM.

up to 0.05 g.

Stirring rate

The stirring rate of the solution is an important parameter that affects the time profile of static headspace. In static headspace the sample solution should be stirred vigorously with a constant rate in all experiments. Figure 3 shows that the relative peak area of acetylene increase by increasing stirring rate. The stirring rate off 400 rpm was considered adequate and was used in all subsequent experiments.

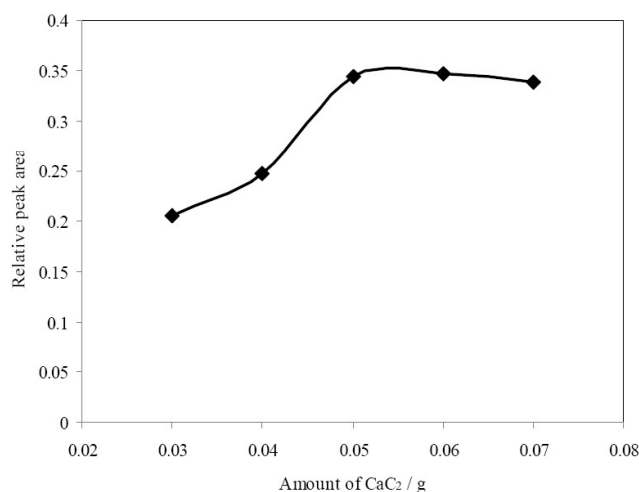


Figure 2 : Effect of amount of calcium carbide on headspace extraction of acetylene. conditions: volume of sample: 7.0 mL, volume of toluene (internal standard): 0.5 mL, stirring rate: 300 RPM, temperature: 30 °C

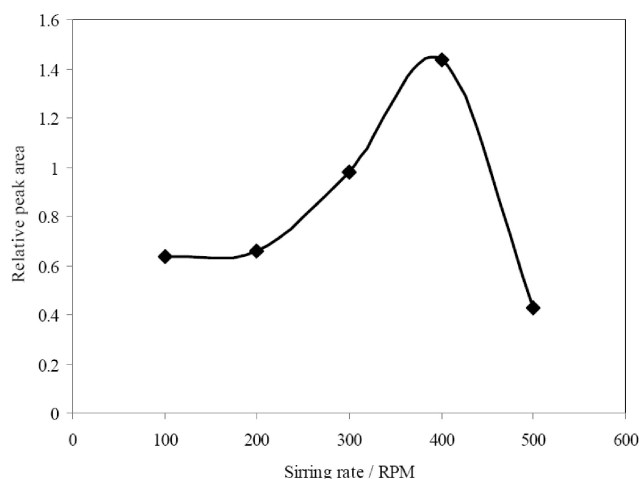


Figure 3 : Effect of amount of stirring rate on headspace extraction of acetylene. conditions: volume of sample: 7.0 mL, volume of toluene (internal standard): 0.5 mL, amount of calcium carbide: 0.05 g, temperature: 38 °C

Analytical performance

Seven organic solutions (7.0 mL) containing water

from 100.0 to 1000.0 mg L⁻¹ (0.01 to 0.1%) were submitted to the whole analytical procedure. The peak area of the acetylene relative to toluene, as an internal standard, was used for quantitative analyses. The results obtained showed that linearity were excellent for water with correlation coefficient of 0.9947 which indicates that a good linear regression was established.. The limit of detection (LOD) and the limit of quantification (LOQ) were calculated using the following equations:

$$\text{LOD} = \frac{3S_b}{m}$$

$$\text{LOD} = \frac{10S_b}{m}$$

where S_b = the standard deviation (SD) of the response and m = the slope of the calibration plot. The S_b is normally obtained from the SD of the blank sample. As it is impossible to obtain a sample without water, the first point of the calibration plot, where no added water is used as the blank sample and its SD was used as S_b . The slope was obtained from the regression analysis of water. The limit of detection (LOD), and the limit of quantification (LOQ) were 54 and 181 mg L⁻¹, respec-

TABLE 1 : Figure of merits obtained for water content in organic solvent (xylene) determination

Equation	Coefficient of variation	LOD (mg L ⁻¹)	LOQ (mg L ⁻¹)
Area = 0.0067 C + 1.5041	0.9947	54	181

TABLE 2 : Recovery of water obtained from proposed method for dried organic solvent samples

Sample	Certified value / mg L ⁻¹	Water found / mg L ⁻¹	Recovery % ±RSD%
Para-xylene	200.0	210	105 ± 6
	1000.0	901	90 ± 1
Heptane	200.0	208	104 ± 6
	1000.0	909	91 ± 2
isooctane	200.0	196	98 ± 5
	1000.0	1007	101 ± 1

TABLE 3 : Detection of water content in 11 organic solvent (protic and aprotic) using proposed method

Sample	Water / mg L ⁻¹
Para-xylene	< LOD
Cyclohexane	< LOD
Heptane	< LOD
Methyl ethyl ketone	59
Heptane	< LOD
Benzene	< LOD
Iso-octane	< LOD
1-propanol	835
Amyl alcohol	< LOD
Methanol	600
1-butanol	< LOD

tively.

The performance of the method was evaluated

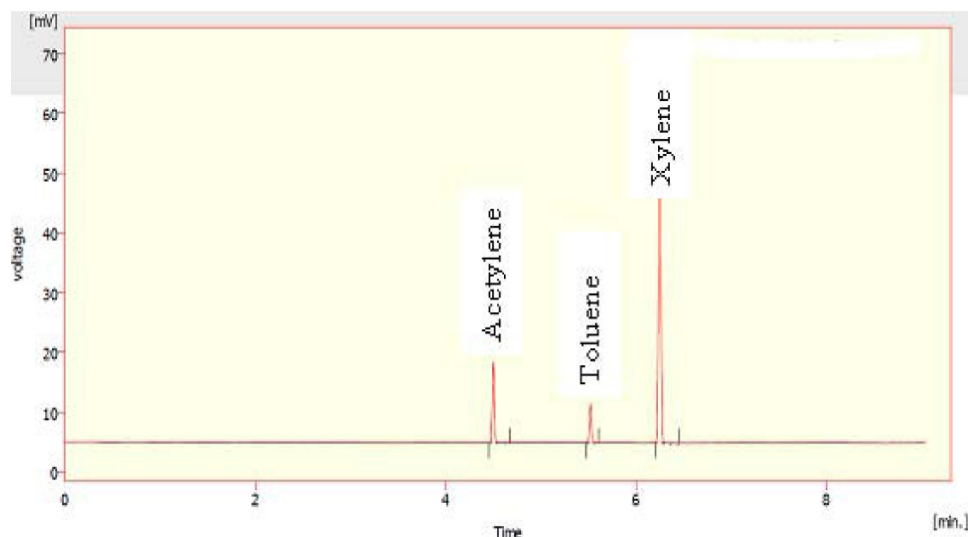


Figure 4 : Typical chromatogram obtained by headspace gas chromatography via reaction of water content with calcium carbide in paraxylene solvent

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through the analysis of different organic solvents and a recovery study was performed spiking samples with the analytes at two different concentrations (200.0 and 1000.0 mg L⁻¹). The average recovery values ranged from 90 to 105% as can be seen in TABLE 2. The inter-day relative standard deviations (repeatability) resulting to be in the range from 4-6% and 1-2%, respectively (TABLE 2). The intra-day relative standard deviations (repeatability) resulting to be in the range from 9-13% and 9-15%, respectively. As shown, satisfactory results were obtained in the recovery tests. Chromatograms of water content of xylene after reaction with calcium carbide (acetylene) spiking at the concentration level 100.0 mg L⁻¹ is shown in Figure 4.

CONCLUSION

Headspace extraction provides a simple, low-cost alternative method for the analysis of water content in organic solvents after reaction of water and calcium carbide.

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