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INDIRECT METHOD FOR THE DETERMINATION OF WATER USING HEADSPACE GAS CHROMATOGRAPHY

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SUMMARY

    This research investigated an analytical method for the quantitative determination of water using headspace gas chromatography (HSGC) and the reaction of calcium carbide and water to produce acetylene. Samples containing water were transferred to a dry vial containing calcium carbide, after which the vial was sealed. The acetylene which formed inside of the vial was then measured by HSGC and used to calculate the original concentration of water in the sample.

    The investigation indicates that the method is a viable alternative for the determination of water in various organic solvents, for concentration ranging from 60 to 400 ppm (μl l^{-1}).

INTRODUCTION

    The reliable determination of water in solid, liquid and gaseous materials is an important part of many chemical operations. Both large- and small-scale processes might be adversely affected by small amounts of water. Its presence in a reaction medium might significantly alter the speed or course of a reaction, or contribute to the degradation of a product. Consequently, a significant amount of research has been devoted to the development of new and better methods for determining water.

    The Karl Fischer titration is one of the most popular techniques for water determinations. This widespread recognition is as good a testimony as any to the great utility of this technique. But there are certain chemical interferences which make the Karl Fischer titration unsatisfactory for certain applications[1,2].

    Gas chromatography (GC) has been investigated as an alternative technique for water determinations. Direct measurement of trace concentrations of water by GC has been complicated by two factors, however. The extremely polar nature of the water molecule made it difficult to chromatograph prior to the introduction of porous polymers as packing materials for GC[3,4]. The lack of a sensitive detector for water also posed a problem, but advances with the helium ionization detector have made direct gas chromatographic determinations a more viable alternative[5,6].

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Chemical conversion of water to acetylene followed by gas chromatographic determination of the acetylene is a technique that has been used for indirect measurements of water. Samples containing water are brought into contact with calcium carbide. The water and calcium carbide react to form acetylene, a compound

$$2H_2O + CaC_2 \rightarrow C_2H_2 + Ca(OH)_2$$
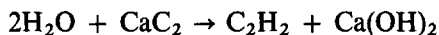
with a very favorable response using a flame ionization detector. The acetylene is measured, and the amount of water originally present in the sample can then be calculated.

This technique has been employed in different ways, but the most prevalent is the use of a pre-column of calcium carbide in the gas chromatograph itself[7,8]. The use of the pre-column has enabled some researchers to determine water down to the 5–10 ppm (μl l^{-1}) range, but long turnaround times for sample analysis and the need for frequent replacement of the pre-column make this an unattractive alternative for routine applications.

This research has investigated the possibility of using the calcium carbide–water reaction in a different fashion. The sample containing water is transferred to a dry vial containing calcium carbide. The acetylene is formed inside the sealed vial and determined using headspace gas chromatography (HSGC). This variation offers the advantages of a faster turnaround time for sample analysis and the potential for completely automated analysis, using one of the commercially available Automatic Head Space Samplers.

EXPERIMENTAL

Apparatus

A Hewlett-Packard Model 5880A gas chromatograph and terminal, equipped with a flame ionization detector was used for the analysis. The separation was accomplished with a 6 ft. × 0.25 in. (4 mm I.D.) glass column with a packing of 5% SE-30 on Porapak Q (80–100 mesh) (Waters Chromatography Division, Millipore, Milford, MA, U.S.A.). The headspace samples were injected manually with a gas-tight precision sampling syringe (Series A-2, 2.0 ml) available from Precision Sampling Corp. (Baton Rouge, LA, U.S.A.). The sample reaction and subsequent headspace equilibration was completed in 50-ml glass reaction vials available from Supelco (Bellefonte, PA, U.S.A.). The vials were sealed with septa of brominated butyl rubber, obtained from The West Co. (Phoenixville, PA, U.S.A.), and aluminum seals, Wheaton Scientific (Millville, NJ, U.S.A.).

Reagents

Methanol, ethanol, 2-propanol, toluene, hexane, methylene chloride and acetonitrile, all reagent grade, were purchased from J. T. Baker (Phillipsburg, NJ, U.S.A.). Calcium carbide (10–40 mesh) was obtained through Fisher Scientific (Fair Lawn, NJ, U.S.A.).

RESULTS

Sample preparation

With the practice of headspace analysis (HSA) one usually conducts some preliminary tests with samples prepared in the laboratory to optimize or troubleshoot some of the experimental variables. The nature of this project (indirect determination of water) was different than most other HSA application. It involved chemical conversion of the analyte into another form within the head space vial. This meant that sufficient time had to be allowed for the conversion reaction to occur, as well as the equilibration of the product between the vapor and liquid phases. Consequently, many of the HSA variables could not be evaluated until some other aspects of the sample preparation procedure were understood.

Potential sources of contamination were also an important aspect to consider. All glassware, solvents or other equipment must be made as anhydrous as possible. It is not always practical to eliminate all of the water from these sources. Many solvents, for instance, are particularly difficult to completely dry (*i.e.*, the lower chain alcohols). Once they are anhydrous, one must be concerned with further contamination from atmospheric moisture. A practice which is frequently used with water determination methods is to measure the amount of water in a blank solution which has been handled in a manner similar to samples or standards. The amount of water found in the blank solution is then subtracted from the total amount of water found in the samples or standards. So the emphasis is not on completely eliminating the water in the solvents, but rather on attaining as low and reproducible a level of water as possible.

In a similar vein, we found that it would be difficult, time consuming and impractical to add a constant amount of calcium carbide to several headspace vials and eliminate all of the acetylene which forms before analyte is added. Thus, an excess but not necessarily a constant amount of calcium carbide was always added. The goal then changed to decreasing the amount of background acetylene to as low a reproducible level as possible.

Headspace vials and septa. Some preliminary experiments on headspace vial preparations were done by adding only calcium carbide to the vials, sealing them, and measuring the amount of acetylene produced. Before using the vials they were dried in a vacuum oven overnight at a temperature of 250°C, and then cooled in a desiccator over indicating Drierite. The calcium carbide was taken from its storage container and measured into a small plastic cup which held 1 g of the material. The calcium carbide was then transferred to the vial, and the vial was purged with a stream of dry nitrogen. It was hoped that this nitrogen purge would eliminate any acetylene formed on transfer of the calcium carbide from the storage container to the headspace vial. Following the purge, the vials were sealed with the septa and equilibrated in a water bath at 32°C. Initially, the septa used in the experiments were stored in a desiccator overnight. It was then discovered that these septa could be dried in an oven at temperatures of 120°C for short periods of time with no deleterious effects. Some simple drying experiments were performed on the septa. The results of these experiments, listed in Table I, indicate a significant decrease in the concentration of acetylene in the vial as the drying conditions become more rigorous (*i.e.*, oven drying). This would seem to indicate that the septa adsorb and/or absorb a certain amount of moisture, which can then migrate into the dry headspace vial and form acetylene. Drying the septa at 120°C improves the

TABLE I

SEPTA PREPARATIONS

$n = 9$ measurements.

Preparation technique	Average acetylene peak area
(1) Overnight desiccation	$100 \cdot 10^3 \pm 17 \cdot 10^3$
(2) 30 min at 120°C	$64 \cdot 10^3 \pm 18 \cdot 10^3$
(3) 60 min at 120°C	$60 \cdot 10^3 \pm 20 \cdot 10^3$

situation significantly. Drying times over 1 h were not attempted since the septa began to melt and deform after a period of 1 h.

Calcium carbide transfers. To evaluate potential interferences introduced in the handling of the calcium carbide, some additional tests were conducted. Calcium carbide was added to each of 20 vials after which they were purged with dry nitrogen for a period of 5 min, sealed and equilibrated overnight. A second set of 20 vials were prepared. These headspace vials, septa and calcium carbide were placed in a glovebag which was purged with dry nitrogen. The calcium carbide was transferred to all of the vials and the septa put in place. The vials were then removed from the glovebag and the septa sealed with the aluminum caps. These vials were also equilibrated overnight. The acetylene was then determined in all of the vials.

The average acetylene peak area in the vials obtained by the two transfer techniques are listed in Table II. Comparison of the results indicate that the use of the glovebag would be more desirable in two respects: (i) the amount of acetylene produced is significantly reduced when the transfers are carried out in a glovebag, and (ii) the standard deviation of the results for the glovebag is lower, indicating that these vials can be prepared in a more reproducible manner.

A plot of the peak areas obtained from the analysis of the individual vials *versus* the vial number is shown in Fig. 1, with the vial number referring to the order which the calcium carbide was added to the vials. From this graph, one can see that the peak areas for both techniques begin at approximately the same values for the first few vials. As the vial number increases, the magnitude and scatter of the data for the vials prepared using the nitrogen purge increases significantly in comparison with the results with the glovebag. Consequently, all transfers of calcium carbide for subsequent studies were done using the glovebag technique.

TABLE II

COMPARISON OF TRANSFER TECHNIQUES

$n = 20$ measurements.

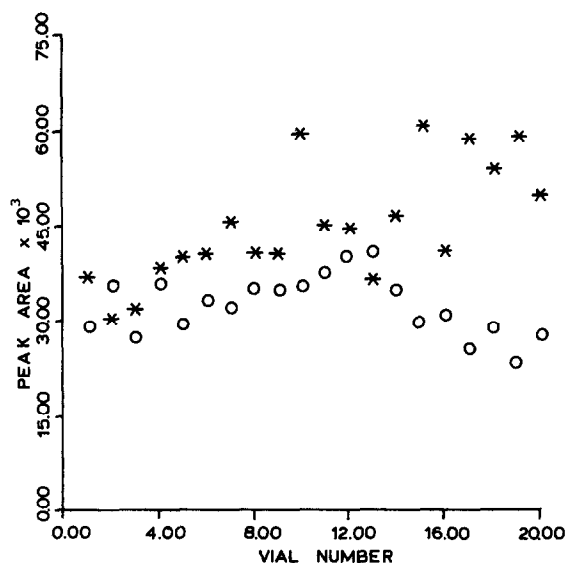| Transfer technique	Average acetylene peak area (counts)	Standard deviation (counts)
Glovebag	$33 \cdot 10^3$	$4 \cdot 10^3$
Nitrogen purge	$45 \cdot 10^3$	$9 \cdot 10^3$

Fig. 1. Graphical comparison of calcium carbide transfer techniques. (○) Glovebag; (*) nitrogen purge.

Determination of water in solvents

Different aspects of the calcium carbide–water reaction, such as reaction times and interfering or non-specific reactions, had to be understood before the technique could be successfully applied to the determination of water. Control of the parameters which affected the HSA was important as well (*i.e.*, equilibration time, equilibration temperature and sample matrices). The successful evaluation of any one of these variables could be very dependent on the control of many others.

Adequate preparation of the solvents used in the proposed technique can have a significant effect on the reliability of the results obtained. Using reagent grade solvents with no preparations could mean working with blank solutions which might contain 300 ppm (μl l^{-1}) of water or more. To do a water determination at or below the 100 ppm (μl l^{-1}) level, the error introduced by a blank which is at least three times larger than the sample could be significant; especially when considering all of the other variables which need to be controlled. Consequently, all solvents were dried with either molecular sieves or a combination of anhydrous calcium sulfate for a preliminary treatment followed by molecular sieves. Measures were also taken to ensure that all glassware was as dry as possible and that all solutions were handled in a consistent manner. This was to prevent any contaminations from atmospheric moisture.

Reaction times and temperatures. To study the reaction times, headspace vials were prepared as described in the previous sections. Several blank solutions of 2-propanol and solutions spiked with water to a concentration of 100 ppm (v/v) (μl l^{-1}) were prepared. Aliquots of 10 ml of either a blank or spiked solution were added to a series of prepared headspace vials. Some of the vials were shaken by hand (both spiked and blank solution) and others were shaken mechanically. All of the vials were equilibrated in a water bath at 32°C for a measured period of time. After the equilibration, the headspace of a vial containing a blank solution was analyzed

TABLE III

RESPONSE FACTOR FOR 2-PROPANOL SOLUTIONS SPIKED WITH WATER

$$\text{Response factor} = \frac{\text{area counts (spike)} - \text{area counts (blank)}}{\text{spike concentration (ppm water)}}$$

Conditions	Reaction time	Response factor (counts/ppm)
Hand shaking (1 min)	100 min	311
Mechanical shaking (1 min)	30 min	154
Mechanical shaking (1 min)	75 min	1384
Mechanical shaking (1 min)	100 min	1226
Hand shaking (1 min)	18 h	2785

followed by that of a spiked solution. Results were erratic and it appeared that complete conversion of all water in a vial would take several hours. Ten blank and ten spiked vials were prepared in the same manner and allowed to equilibrate for a period of 18 h (overnight). The headspace analysis of these vials resulted in a significant increase in the peak area of acetylene for spiked solutions compared to the blank solutions. Table III lists the response factors found for different reaction times as well as different shaking methods.

   The results in Table III show a response factor which almost doubles with an 18-h reaction period. Fig. 2 shows a plot of the acetylene peak areas versus time (following overnight reaction) for vials containing either the 60-ppm spiked solution or the blank solution. The x-axis on the graph refers to the time following the analysis of the first vial. The fact that the acetylene peak areas for both the blank and spiked
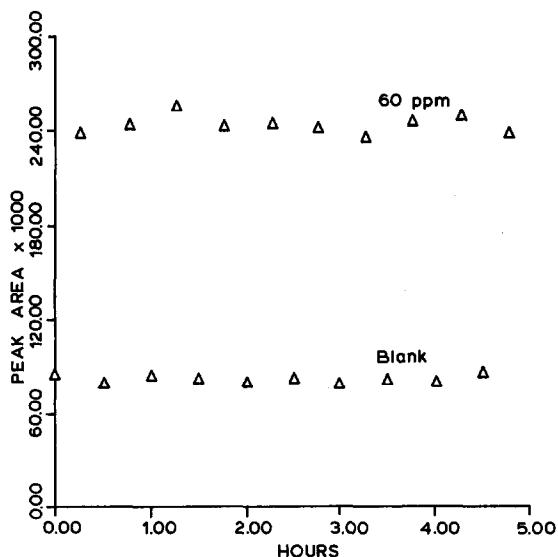

Fig. 2. Plot of acetylene peak areas for spiked and blank solutions of 2-propanol versus time (after 18-h reaction time).

solutions remain farily constant over a 5-h period indicates that reaction of all of the water is complete. Shaking times had an effect with shorter reaction periods but were not studied for the overnight reaction, as it appeared the conversion was complete.

It is very possible that the reaction would be complete in less than 18 h, but this aspect was not investigated. Overnight reaction proved satisfactory and was used in the remainder of the research. In terms of completing an experiment, it was more practical to prepare a large number of samples one day and complete the headspace analysis the following day. With an automated headspace analyzer, ith might be more practical to implement a shorter reaction time.

The temperature of the water bath in which the vials were equilibrated was varied to determine if there was any effect on the response factors. The study was conducted at two other temperatures; *i.e.* 26°C and 41°C. There was no change in the response factor which was obtained at 32°C, and all subsequent work was done with an equilibration temperature of 32°C.

Determinations of water in 2-propanol. Solutions of 2-propanol spiked with known amounts of water were used for the investigations for the quantitative measurements. Calibration curves were prepared and reproducibility studies performed using different volumes (*i.e.* 5, 10 and 15 ml) of solvent added to the 60-ml headspace vial. These experiments helped in determining the limitations of the technique in terms of accuracy and precision, as well as evaluating the effects of increasing solvent volumes added to the headspace vials. Fig. 3 illustrates the calibration curves.

The increase in slope of the calibration curve accompanying the increase in solvent volume is to be expected. Adding 5.0 ml of a given concentration to one vial and 10.0 ml of that same concentration to another vial would mean that twice the amount of water is added to the second vial. Looking at the change in slope of the lines
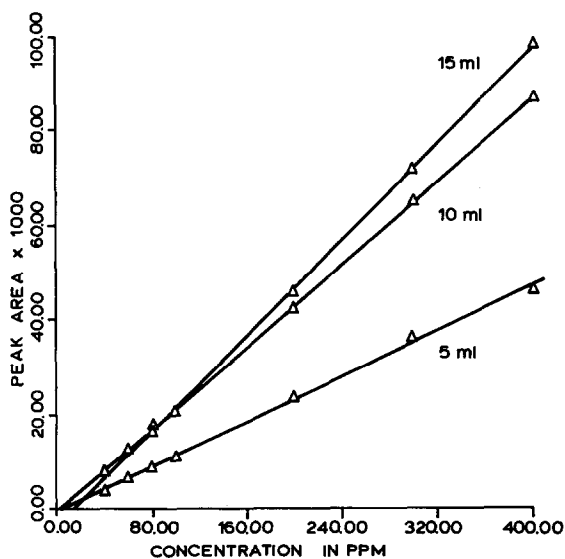

Fig. 3. Calibration curves of water in 2-propanol for increasing liquid phase volumes.

as related to the change in solvent volume, one can see that doubling the volume does not double the slope of the line. This would be due to a certain portion of the acetylene remaining as a solute in the liquid phase. Even though more acetylene is produced and a smaller headspace volume is present, the increased amount of liquid phase will retain more of the acetylene.

To assess the accuracy and precision which could be expected with the actual measurement of water in a sample, some additional experimentation was done with 2-propanol. A solution spiked with water was prepared and treated as a sample whose water content was to be determined. Two different calibration standards, whose water concentrations bracketed that of the sample solution, were also prepared. All three of the solutions were then analyzed by the calcium carbide technique. The peak areas of the standards were used to calculate a response factor, which was then used to experimentally determine the water concentration of the sample solution. The concentration of water in the sample solution was then determined from the average of ten measurements, and compared to the "true" concentration of the solution. The uncertainty of these measurements was also computed.

The sample solution concentrations were studied in the range of 80 to 400 ppm (v/v) ($\mu l\ l^{-1}$). The volume of solvent added to the vial was also varied (5.0, 10.0 and 15.0 ml) in an attempt to find the optimum solvent volume for practical applications. The results of these experiments are listed in Table IV.

The accuracy of all of the experimental results is high. The percent error of all but four of the results was 1% or lower. But there are some discrepancies in the precision of the results obtained for a given concentration determined with different liquid phase volumes. Looking at the values listed in Table IV, one can see that only those

TABLE IV

DETERMINATIONS OF WATER IN 2-PROPANOL

True conc. ppm (v/v)	Exptl. conc.* ppm (v/v)	% Error	R.S.D. (%)
5.0 ml liquid phase volume			
80	82	2.50	13.13
200	197	1.50	9.58
300	308	2.67	4.51
400	400	0	4.51
10.0 ml liquid phase volume			
80	80	0	2.59
100	102	2.00	4.89
200	201	0.50	3.98
300	303	1.00	3.19
400	396	1.00	1.77
15.0 ml liquid phase volume			
80	80	0	7.13
100	100	0	4.65
200	199	0.50	3.42
300	300	0	3.58
400	396	1.00	5.38

* Average of 10 determinations.

determinations done using a 10.0-ml solvent volume furnish relative standard deviation (R.S.D.) values which are all below 5%. For the 15.0-ml volume, one of the R.S.D. values is above 5%. With the 5.0-ml volume, two of the values are above 5%.

Some of these trends in the precision are actually as expected. Referring back to Fig. 3 the plots indicate that the response factor increases as the solvent volume in the headspace vial increases. If one assumes then, that the errors introduced in the procedure remain constant (i.e., sample preparations, the headspace analysis and the conversion of water to acetylene), one should expect that as the solvent volume is increased, lower concentrations could be determined with better precision. The results are as expected when the solvent volume is increased from 5.0 to 10.0 ml, but not for the increase of 10.0 to 15.0 ml. It is quite likely that the overnight reaction is insufficient for the 15.0-ml solvent volume, but longer reaction time were never investigated. The change in the response factor going from the 10.0- to the 15.0-ml volume is not that large, and the possible benefit of a marginal improvement in the precision is not worth a longer turn around time for sample analysis.

From a practical standpoint, the actual level at which a determination is being done and the precision needed in the analysis should dictate the volume of solvent to be used. For the remainder of this research, 10.0-ml liquid phase volumes were added to the headspace vials. But for other applications, the 5.0-ml solvent volume might be appropriate. Using one half the amount of a sample which is limited in supply can be a definite advantage. There appears to be no advantage at all to using a 15.0-ml solvent volume with the conditions used in these experiments.

Determinations of water below 80 ppm ($\mu l \, l^{-1}$). To get a feel for the level of precision which could be expected at lower concentration levels, additional measurements were performed using 2-propanol, methylene chloride, acetonitrile, hexane and toluene. Calibration curves for acetonitrile and methylene chloride were prepared as a check with solvents other than 2-propanol. The results of these studies, listed in Table V, indicate a linear response for the concentration ranges [0–80 ppm ($\mu l \, l^{-1}$)] studied.

Spiked [60 ppm ($\mu l \, l^{-1}$) or lower] and blank solutions were then prepared using all of the solvents. There were four vials prepared containing the solvent blank and seven containing the spiked solutions. The analyses were then completed on all of the vials and the net peak areas determined for each concentration. The relative standard deviation of the measurements at each concentration were calculated and can be found in Table VI along with the response factors obtained for each solvent.

Poor precision was obtained for all determinations at the 20-ppm ($\mu l \, l^{-1}$) level, with the R.S.D. values being well over 10% for all of the solvents. All determinations at the 40-ppm level have an R.S.D. below 7% except toluene. The results obtained at the 40-ppm level might be acceptable under some circumstances, but it would have to be considered the limit for the practical application of the technique.

TABLE V

LINEARITY STUDIES

Solvent	Slope	Intercept	Correlation coeff.
Acetonitrile	1716	2685	0.998
Methylene chloride	1619	−7	1.000

TABLE VI

DETERMINATIONS OF WATER BELOW 60 ppm

Solvent	Conc. (ppm)	R.S.D. (%)	Response factor (counts/ppm)
2-Propanol	60	3.55	2871
	40	6.51	
	20	14.63	
Acetonitrile	60	4.76	1862
	40	5.29	
	20	13.80	
Hexane	41	6.82	1525
	22	18.18	
Methylene chloride	57	6.26	1317
	23	18.51	
Toluene	40	8.64	1720
	20	30.79	

The change in the response factors for the different solvents is interesting in that it probably reflects a change in the distribution coefficient of acetylene in the different solvents. The increased response factor for 2-propanol does not result in any profound benefits in terms of the precision which is achievable at lower concentration levels.

CONCLUSION

The primary objective of the research was the development of an analytical method which could be used for the quantitative determination of water. Initial investigations were undertaken with 2-propanol to optimize the calcium carbide technique and gain some insight into its limitations. Concentrations ranging from 60 to 400 ppm (μl l^{-1}) of water in 2-propanol were measured accurately, with an R.S.D. below 5% for ten individual determinations. The technique was also useful for the determination of water in toluene, methylene chloride, hexane and acetonitrile. Measurements at 60 ppm (μl l^{-1}) typically had a relative standard deviation ranging from 5 to 7%. Determinations below 60 ppm (μl l^{-1}) for all of the solvents had poor precision.

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