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Journal of Chromatography A, 1093 (2005) 212–216
JOURNAL OF CHROMATOGRAPHY A
www.elsevier.com/locate/chroma

Short communication

Determination of acidic and basic species by headspace gas chromatography

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Received 5 August 2005; received in revised form 24 August 2005; accepted 29 August 2005
Available online 9 September 2005

Abstract

This paper reported a novel headspace gas chromatographic (GC) technique on quantification of acidic and basic species. It is based on an acid–base reaction between the measured species and bicarbonate in an aqueous solution, which generates carbon dioxide in a closed headspace sample vial. By operating at 60 °C, carbon dioxide is completely released to the headspace and thus can be measured by GC with a thermal conductivity detector. Bicarbonate concentrations of 0.030 and 0.0025 mol/L are recommended for general applications and very small species content, respectively. This method is able to accurately measure small sample sizes (down to few milligrams or microliters). The present method is simple, accurate, and automatic.
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Keywords: Acid–base; Headspace; Gas chromatography; Thermal conductivity detector; Carbon dioxide; Bicarbonate

1. Introduction

To quantify acidic or basic species, the volumetric titration method is widely used in the laboratories. The titration end-point is usually determined by either a type of pH indicator or pH electrode. In general, the titration method provides excellent measurement precision in the quantification of acidic or basic species due to a sharp pH change at the end-point. Unfortunately, very diluted weak acid or base samples, or extremely low concentrations of strong acids or bases, cannot be accurately measured by titration method because they lack a distinct end-point. The titration method is usually performed in a beaker, where the titrated species is dissolved in an aqueous solution with a fairly large volume. If the sample size is very small, a dilute sample solution will be prepared for the titration. In such a case, even strong acidic or basic species cannot provide a distinct change at the end-point, thus obtaining poor measurement precision and accuracy.

Headspace gas chromatography (HS-GC) has been widely used for analysis of volatile species in complex matrix samples. Many applications based on HS-GC have been published in textbooks [1–3] and review articles [4–7]. In a previous work [8], we have developed a phase reaction conversion (PRC) HS-GC technique for quantifying the nonvolatile species, e.g., carbonate and sulfide in the samples. In this method, sulfuric acid was used as a reaction agent for converting carbonate into carbon dioxide and sulfide into hydrogen sulfide. Both species are volatile and can easily be measured by GC with a thermal conductivity detector. We have also explored a HS-GC method for quantification of carboxyl groups in wood fibers [9] based on the PRC headspace GC technique.

In this work, we present an alternative method for quantification of acidic species using HS-GC applications. The present method is simple, accurate, and automated. It also has the capability to measure the species content if only a very small sample size is available.

2. Experimental

2.1. Chemicals

All chemicals used in the experiment were from commercial sources. Two standard bicarbonate solutions consisted of sodium bicarbonate, 0.030 and 0.0025 mol/L, respectively, each with

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doi:10.1016/j.chroma.2005.08.079

0.1 mol/L sodium chloride. A 0.1000 mol/L standard hydrogen chloride acid (HCl) solution was made through volumetric dilution based on a 1.000 mol/L HCl solution from VWR Scientific (West Chester, PA, USA).

2.2. Apparatus and operation

All measurements were carried out using an HP-7694 Automatic Headspace Sampler and Model HP-6890 capillary gas chromatograph equipped with a thermal conductivity detector (Hewlett-Packard, now Agilent Technologies, Palo Alto, CA, USA). GC conditions were: a porous-wall, large-diameter capillary column coated with divinylbenzene homopolymer (model GS-Q, Agilent Technologies, Palo Alto, CA, USA) was used and operated at 30 °C; carrier gas helium flow rate of 3.1 mL/min. Headspace Sampler operating conditions were: oven temperature of 60 °C; vial pressurized by helium and pressurization time of 0.2 min; sample-loop fill time of 0.2 min; loop equilibration time of 0.05 min; the vial equilibration time is 2 min for liquid sample and 10 min for solid sample analysis.

The sample preparation and measurement procedures were as follows:

(1) For basic species analysis, a given amount of sample (liquid, V_b or solid, w), is added in a given volume of a 0.100 mol/L HCl standard solution (V_a) for neutralization reaction. Then a given volume of the resulting solution is injected by a micro-syringe into a sealed headspace sample vial which contains 4 mL of standard bicarbonate solution.
(2) For acid sample solution analysis, a given volume of the solution is directly injected by a micro-syringe into a sealed headspace sample vial which contains 4 mL of standard bicarbonate solution.

After adding the sample, the headspace sample vials are placed in the headspace sampler tray for automatic HS-GC measurements. The headspace sample vial is shaken vigorously at an equilibration temperature before GC headspace sampling.

3. Results and discussion

Because this work is based on a phase reaction conversion headspace technique to realize an indirect measurement of acidic or basic species, it is important to choose a reagent having a volatile product in the reaction. In this work, bicarbonate was chosen as it generates carbon dioxide gas upon reaction with hydrogen ions, which can be written as

$$HCO_3^- + H^+ \leftrightarrow H_2O + CO_2 \quad (1)$$

Carbon dioxide has a partitioning between the vapor and liquid phase, i.e.,

$$K = \frac{CO_2(g)}{CO_2(aq)} \quad (2)$$

All symbols are defined in Table 1.

Table 1
Symbols and definitions

K	Vapor–liquid partitioning coefficient
$CO_2(g)$	Concentration of carbon dioxide in the headspace (vapor phase)
$CO_2(aq)$	Concentration of carbon dioxide in aqueous solution (liquid phase)
A	GC peak area from TCD detector signal for CO_2 in headspace
$C_{HCO_3^-}$	Concentration of bicarbonate solution (mmol/L)
m_a	Amount of hydrochloric acid HCl (μmol)
A_0	y-Intercept of calibration curve
k	Slope of the calibration curve
C_a	Acid species concentration in sample (mol/L)
V_a	Volume of the standard acid solution (mL)
V_b	Volume of basic solution (mL)
$V_{syringe}$	Sample volume added to the headspace testing vial (μL)
n	Valence of anion in one molecule
C_b	Basic species concentration in liquid sample (mol/L)
x_b	Basic species content in solid sample (%)
C_a^S	Concentration of standard HCl solution (mol/L)
C_a^R	Concentration of residual HCl in resulting solution after neutralization (mol/L)
A^S	GC peak area for HCl measurement in the standard solution
A^R	GC peak area for residual HCl measurement in the resulting solution
w	Weight of the solid sample (g)
F	Molecular weight of the basic species in sample (g/mol)

In this method, the excess amount of bicarbonate is essential in order to achieve a complete reaction with hydrogen ions. Furthermore, other variables must also be taken into account in the quantification analysis.

3.1. Temperature effect

For gaseous species, their corresponding vapor pressure is very high. At a temperature of 60 °C, the dimensionless vapor–liquid partitioning coefficient of carbon dioxide, expressed in Eq. (5), is much greater than 1000 [10], almost completely releasing carbon dioxide from the solution into the headspace, and shifting reaction (1) towards the products. Thus, a quantification analysis can be performed by measuring headspace carbon dioxide content using GC.

It was observed, however, that bicarbonate decomposition takes place at the elevated temperature, which is shown in Fig. 1. The bicarbonate decomposition in aqueous solution can be written as,

$$2HCO_3^- \leftrightarrow H_2O + CO_3^{2-} + CO_2 \quad (3)$$

In Fig. 1, we notice that bicarbonate decomposition is also an equilibration reaction. A complete equilibrium between vapor and liquid phases of carbon dioxide, formed from bicarbonate decomposition, can be achieved in ~8 min in a closed headspace vial at the given conditions. Approximately, 10% of the bicarbonate is decomposed. Consequently, carbon dioxide formed due to bicarbonate decomposition may affect the measurement accuracy on the species of interest, especially for a sample with very low acid content. The decomposition is directly proportional to the bicarbonate concentration, which is described by

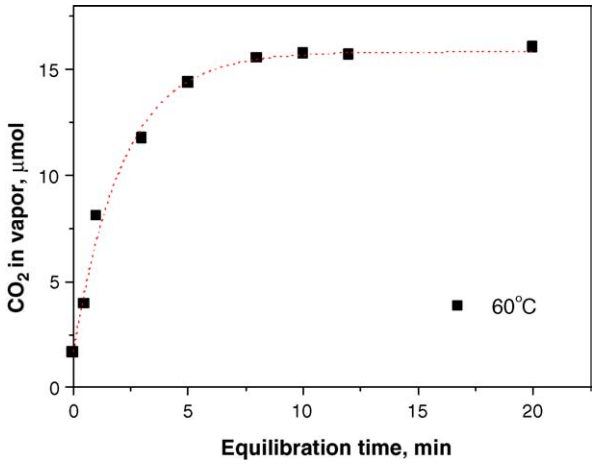

Fig. 1. Carbon dioxide generated by bicarbonate decomposition as a function of equilibration time.

the equation

$$A = -1.20(\pm 4.86) + 3.01(\pm 0.04)C_{HCO_3^-} \quad (4)$$

with eight data points ($n = 8$) and a squared regression value (R^2) of 0.9990 at a 95% confidence level.

Thus, the decomposition effect can be minimized by either choosing a short equilibration time, as shown in Fig. 1, or using a lower bicarbonate content solution, shown in Eq. (4). At very low bicarbonate concentrations, the amount of carbon dioxide produced by the decomposition reaction will be relatively low compared with that formed by the reaction with the sample species. Thus, the measurement accuracy can be improved.

In choosing an operating temperature for the system, we considered previous problems of fouling in the GC column due to water vapor. Since the GC column is operating at 30 °C, any water vapor entering the column will condense, which may affect the column separation performance. Thus, the temperature of 60 °C was chosen as compromise between reducing carbon dioxide solubility (high temperature) and minimizing water vapor in the headspace (low temperature).

3.2. Reaction time

It was observed that the reaction is rapid in a homogeneous reaction system. However, a longer reaction time is required in the heterogeneous reaction system. For example, we found that the determination of carboxylic acids in wood fibers requires ~10 min at a temperature of 60 °C in order to achieve a complete reaction [9].

3.3. Effect of carbon dioxide from air

Because the present method is based on carbon dioxide measurement through HS-GC, the carbon dioxide in air affects the accuracy of the method. A simple and practical way is to perform a blank testing to obtain the signal caused by the given volume of air in the headspace at the same experimental conditions. The effect of carbon dioxide in air can thus be corrected through a calibration.

3.4. Liquid sample size

In general, measurement sensitivity can be improved by adjusting the sample size introduced into the headspace sample vial. However, excess amount of bicarbonate in the reaction system should be guaranteed. Using the present commercial headspace sampler, variations in the headspace volume can affect the measurement results. Therefore, it is important to avoid a significant change in the headspace volume. If, for example, in a 20 mL headspace testing vial containing a 4 mL bicarbonate solution, a sample size of 200 μL is used, this addition causes a 1.25% change in the headspace volume, which is negligible in the measurement. For a solid sample, the amount of species content in the resulting solution can be adjusted in the solution preparation.

3.5. Calibrations

The calibration curves for this method were generated by the addition of different volumes of 0.1000 mol/L HCl standard solution (using micro-syringe) to both a 4 mL 0.030 mol/L bicarbonate solution and a 4 mL 0.0025 mol/L bicarbonate solution. These solutions were then placed in the headspace testing vial, and the corresponding GC signal peak areas were plotted. The calibration curves are described by their respective equations. For the 0.030 mol/L bicarbonate solution, the equation is

$$A = 80.8(\pm 17.3) + 22.0(\pm 0.5)m_a \quad (5)$$

with eight data points ($n = 8$) and an R^2 value of 0.9974; for the 0.0025 mol/L bicarbonate solution, the equation is

$$A = 9.6(\pm .0.9) + 21.7(\pm 0.3)m_a \quad (6)$$

with six data points ($n = 6$) and an R^2 value of 0.9994.

The curve is approximately linear over a wide range of concentrations. However, at a blank and very low amounts of HCl addition, the curve tails up sharply to a positive, non-zero y-intercept value. As discussed above, this is caused by the bicarbonate decomposition and is significant when the content of the measured species is very low. By increasing the sample size added to the reaction system, we can achieve a higher signal that is located in the linear response range to avoid a serious error obtained at the low concentration range. The calibration curve equations demonstrate that use of low bicarbonate concentration solution greatly reduces the y-intercept value of the blank (9.6 versus 80.8). Therefore, if the sample contains a very low amount of measured species, a solution of low bicarbonate concentration (0.0025 mol/L) is recommended. As shown in Eq. (6), an excellent correlation can still be achieved even in such a low concentration range with a limit of quantification [11] of 0.27 μmol.

The calibration equation can also be expressed as,

$$A = A_0 + km_a \quad \text{or} \quad m_a = \frac{A - A_0}{k} \quad (7)$$

with

$$m_a = C_a V_{syringe} \quad (8)$$

3.6. Determination of acidic and basic species samples

In general, for the solid sample, a sample solution must be prepared prior to HS-GC measurement.

3.6.1. Acid

For liquid samples, a given volume of sample is taken by a micro-syringe and injected into a closed headspace sample vial containing a bicarbonate solution. According to Eqs. (5) and (6), for general applications, 4 mL of a 0.030 mol/L bicarbonate solution is recommended; however, for samples with very low acidic species content, 4 ml of a 0.0025 mol/L bicarbonate solution is recommended. Combining Eqs. (7) and (8), we can calculate the acid species concentration by the following equation

$$C_a = \frac{A - A_0}{nkV_{syringe}} \quad (9)$$

Thus, the required steps for determination of the acidic species are:

- Injection of a given volume into closed headspace sample vial.
- Measurement of GC signal for carbon dioxide.
- Application of this value (A) to Eq. (9) to calculate the acidic species concentration.

3.6.2. Base

For basic sample testing, prepare a solution by adding a given amount of sample into a given volume of a standard HCl solution (e.g., 0.1000 mol/L). The excess amount of HCl is required to achieve a complete neutralization for the basic species introduced. Then, the residual HCl in the resulting solution is measured by HS-GC using the same procedure as described above.

For liquid samples, the residual HCl concentration in the resulting solution after neutralization can be expressed as,

$$C_a^R = \frac{C_a^S V_a - C_b V_b}{V_a + V_b} \quad (10)$$

According to Eqs. (7), (8) and (10), the basic species concentration in the sample can be calculated as,

$$C_b = \frac{C_a^S V_a - C_a^R(V_a + V_b)}{nV_b} = \frac{A^S V_a - A^R(V_a + V_b) + A_0 V_b}{nkV_{syringe} V_b} \quad (11)$$

For solid sample, the residual HCl concentration in resulting solution after neutralization can be written as,

$$C_a^R = \frac{C_a^S V_a - 1000 w x_b / F}{V_a} \quad (12)$$

According to Eqs. (7), (8) and (12), the content of basic species, in weight percentage, in the solid sample can be calculated as,

$$x_b\,(\%) = \frac{(C_a^S - C_a^R)V_a F}{1000nw} \times 100 = \frac{(A^S - A^R)F}{10^4 nkw} \quad (13)$$

Thus, we can quantify the basic species content by measuring the HS-GC peak area on both the standard HCl solution and resulting solution according to Eqs. (11) and (13). Notice that the same volume of the standard solution and resulting solution should be injected into the HS-GC.

Hence, the required steps for determination of the basic species are:

- Addition of basic sample to excess amount of standard HCl solution.
- Allow neutralization reaction to complete.
- Injection of a given volume HCl standard solution and resulting solution, respectively, into the closed headspace sample vials.
- Measurement of GC signals for carbon dioxide of these vials.
- Calculation of basic species concentration using Eqs. (11) or (13), depending on sample phase.

3.7. Method precision and validation

The precision and accuracy of PRC HS-GC measurement by the present commercial system have been evaluated on numerous occasions. We found that the relative standard deviations of the headspace GC measurement are smaller than 0.1% for lab-prepared solutions and 2.0% for

Table 2
Data comparisons between the present and reference methods on three different types of samples

Sample	Hydrogen chloride (mol/L)		Relative difference (%)
	Present method	Titration	
Solution #1	0.1002	0.1000	0.2
Solution #2	0.0498	0.0500	−0.3
Solution #3	0.0247	0.0250	−1.2
Solution #4	0.0101	0.0100	1.0
	Sodium carbonate (%)		Relative difference (%)
	Present method	Coulometry	
Black liquor char #1	4.9	4.7	4.3
Black liquor char #2	23.2	24.1	−3.7
Black liquor char #3	25.1	24.5	2.4
Black liquor char #4	42.0	42.8	−1.9
	Carboxylic acids in pulp (μmol/g)		Relative difference (%)
	Present method	Conductivity titration	
Pulp sample #1	78.9	78.6	0.4
Pulp sample #2	68.2	73.9	−7.7
Pulp sample #3	41.3	41.5	0.6
Pulp sample #4	69.5	69.4	0.1
Pulp sample #5	81.5	75.5	8.0
Pulp sample #6	61.1	61.0	0.1
Pulp sample #7	22.5	24.1	−6.9
Pulp sample #8	55.7	58.1	−0.7

industry liquor [8], and 4% for heterogeneous systems [9], respectively.

Validation was accomplished by three types of samples, i.e., lab-prepared HCl standard solutions, sodium carbonate in black liquor chars, and carboxylic acids in chemical pulps from pulping and bleaching process, respectively. As shown in Table 2, the relative differences between the present method and reference methods on these samples testing are, <1.2% for the standard HCl solutions, <5% for sodium carbonate in black liquor char samples, and <8% for carboxylic acids in the chemical pulps [9], respectively. These results indicate that the present method is justifiable.

4. Conclusions

A novel headspace GC technique has been developed for the determination of acidic and basic specie concentrations. The significant advantage of this particular method is that it is very accurate for small sample sizes, where the conventional titration method simply does not work. The method is simple, accurate, and automatic.

Acknowledgement

This work was partly supported by the Special Research Funds of Guangxi University.

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