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Analysis of nonvolatile species in a complex matrix by headspace gas chromatography

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Abstract

This study developed a phase reaction conversion (PRC) headspace gas chromatographic (HS-GC) technique for the measurements of nonvolatile species in liquid or solid samples. The technique is demonstrated by the measurements of carbonate in aqueous carbonate solutions and in kraft pulp mill liquor samples. A very small amount of sulfuric acid (volume of 0.5 ml, concentration of 2 mol/l) is used to acidify a sample of less than 300 μl in volume and convert the dissolved carbonate into carbon dioxide (gas) in a sample vial (reactor) that is analyzed by thermal conductivity detection through a headspace sampler. The carbonate concentrations measured by PRC-HS-GC in seven kraft liquor samples agree very well with those measured using a coulometric and a titrametric method. Simultaneous analysis of multiple species was also conducted to demonstrate the versatility of the method. The present method is very simple, rapid, reliable, accurate, and fully automated. It can be applied to analyze other nonvolatile species in various industrial and environmental samples.

Keywords: Headspace analysis; Kraft black liquors; Carbon dioxide; Carbonates; Sulfides

1. Introduction

Headspace gas chromatography (HS-GC) is a powerful technique for the analysis of volatile species in corrosive and complex matrix samples. The basic principle of HS-GC and many useful methods can be found in textbooks [1–3] and review articles [4–6]. Because direct liquid-phase probing is not necessary, HS-GC eliminates the sample matrix effect on measurements. Drozd and Novak [7] developed a standard addition method for HS-GC analysis of solutes in equilibrated gas–liquid systems. The method is based on material balance under standard addition and phase equilibrium in headspace so that the solute concentration in the liquid phase can be derived from two measurements in the vapor phase (headspace) before and after standard addition. Markelov and Guzowski Jr. [8] developed a full evaporation (FE) technique to eliminate the sample matrix effect to analyze analytes in aqueous solutions using HS-GC. The FE-HS-GC method is based on the near-complete transfer of the analyte from the liquid phase to the vapor phase (headspace) by vaporization when a very small amount of the liquid sample is dispensed into a heated sample vial.

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Most of the headspace chromatographic techniques, including those by Drozd and Novak [7] and Markelov and Guzowski Jr. [8], are only suitable for analysis of volatile species and cannot be applied to nonvolatile species. There is a great need for accurate analytical techniques to determine nonvolatile species in complex matrices. A typical example is the determination of carbonate concentration in spent pulping liquors, called weak black liquor because of its color. Weak black liquors contain a large amount of carbonate and various other inorganic salts and organic materials, such as lignin and hemicellulose, with total dissolved solids (TDSs) of around 15%. The analysis of carbonate in black liquors is very important in the preventing of scaling in weak black liquor concentrators or evaporators, a severe problem that affects pulp and paper production. However, it is very difficult to analyze carbonate in black liquors due to its complex sample matrix. Titrametry has failed, although it is frequently used for carbonate analysis in white liquors (regenerated pulping chemical solution from pulp mill chemical recovery cycle, containing mainly hydroxide and sulfide and minor carbonate called dead load) and green liquors (aqueous solution of smelt ash derived from burning of the organic materials during the combustion of concentrated black liquor). The application of capillary ion electrophoresis [9] and ion chromatography [10–12] for carbonate analysis in black liquors requires complicated sample pretreatment. The sensitivity and repeatability of the measurements are poor. The time-consuming coulometric technique [13], though being adopted in commercial analytical laboratories for carbonate analysis in black liquors, presents difficulties and measurement uncertainties due to the interference of other volatile species released during liquor acidification.

To take advantage of the matrix-independent HS-GC analysis, we use chemical reaction to convert (or gasify) the nonvolatile species into gaseous products, so that HS-GC can be applied. From the analysis of the gaseous products, the concentration of nonvolatile analyte in the original sample can be determined based on chemical reaction equations. The objective of the present study is to develop and demonstrate an analytical procedure that can provide accurate and reliable measurements of nonvolatile species in complex matrix samples through the measurements of gas products released during condensed phase conversion reactions by HS-GC. We call this procedure phase reaction conversion headspace gas chromatography (PRC-HS-GC), which follows the term of FE-HS-GC used by Markelov and Guzowski Jr. [8]. We will use carbonate analysis in aqueous sodium carbonate solutions and kraft black liquors as examples to achieve the objective of the present study. More specifically, dissolved carbonate (a nonvolatile species) is converted to carbon dioxide through the acidification of the samples using sulfuric acid in a sample vial (reactor). The carbon dioxide is then analyzed by GC through a headspace sampler. We will also demonstrate simultaneous multiple species analysis using PRC-HS-GC through the measurements of carbonate and sulfide in kraft liquors. We believe that the PRC-HS-GC method is simple, rapid, reliable, and accurate for carbonate analysis in black liquors and also suitable for other applications.

2. Methodology

2.1. The phase reaction conversion technique

It is a common practice in analytical chemistry to indirectly determine an unknown analyte in a complex matrix through the measurements of the products of chemical reactions involving the analyte. Phase reaction conversion (or gasification) headspace gas chromatography is based on a conversion of a fixed percentage (or a constant rate), including complete conversion, of an unknown analyte from a condensed phase in a sample. The sample may be either a liquid or a solid that is converted into the gas phase through chemical reactions. The analyte is then determined through the measurements of the gas products using HS-GC. The term ‘‘fixed percentage’’ here means that the conversion can be incomplete, but the final condensed phase conversion rate is a constant; therefore, quantitative analysis of the analyte in a condensed phase can be achieved through calibration. For simplicity in mathematical derivation of the PRC-HS-GC technique, the following one-step reaction is assumed for the phase conversion reaction process:

$$rR + bB(\text{condensed}) \leftrightarrow pP + qQ(\text{gas}) \quad (1)$$

where B is the analyte to be determined in a sample. It is further assumed that the conversion rate of a nonvolatile compound B to a gaseous species Q is α (≤ 1) when it reacts with another reactant R (externally added, preferably liquid, dissolving in a liquid if it is a solid). The chemical reactions take place in a sample vial, as the reactor, of volume V_T. The initial volume of the unknown sample that contains analyte B added in the reactor is V_S. The final total volume of all the condensed phase species in the reactor after the completion of the chemical reactions is V_L. Then the numbers of moles of product gas Q formed at the completion of reaction (1) in the reactor (sample vial) can be expressed as:

$$n_Q = \alpha \cdot \frac{C_B V_S q}{b} = C_Q(V_T - V_L) \quad (2)$$

where C_B is the molar concentration of the condensed analyte B in the original sample solution to be determined. C_Q is molar concentration of the product gas in the headspace at the completion of the reaction. $V_T - V_L$ is the postreaction headspace volume. From Eq. (2), we have:

$$C_B = \frac{1}{\alpha} \cdot \frac{b}{q} \cdot \frac{V_T - V_L}{V_S} \cdot C_Q \quad (3)$$

2.2. Calibration

External standards are recommended for calibration in using PRC-HS-GC to avoid unnecessary complications by potential chemical reactions. Most commercial HS-GC systems use an inert gas to pressurize the sample vial to create a pressure head to sample the gas in the headspace. The pressurization by the inert gas dilutes the analyte gas in the headspace to be transferred to the sampling loop for GC analysis, which not only affects measurement sensitivity, but also creates complications and uncertainties in calibration, because the dilution ratio used in calibration over that used in an actual individual testing headspace experiment is an unknown. Therefore, liquid standard calibration is often preferred, in which the same headspace dilution ratio (or unity ratio of dilution) can be assumed for both the calibration and individual testing experiment as long as the initial total volume of the samples is the same. In PRC-HS-GC, the unity ratio of dilution is always only an approximation even when exactly the same sample containing analyte B is used in calibration. The analyte dilution in the headspace depends on the postreaction headspace volume $V_T - V_L$ and the total amount of products Q and P formed (if P is also a gas), which all vary with the amount of analyte B contained in a sample. When the calibration sample is not of the same composition as the testing sample, different products may be produced during calibration and testing, further violating the assumption of a unity ratio of dilution. However, when a very small sample is used, the unity ratio of dilution is a valid assumption, as will be demonstrated in this study.

Because the product gas concentration C_Q in the headspace is proportional to the detector signal peak area, e.g., $C_Q = k'A$, the concentration of the analyte B in the sample can be found from Eq. (4):

$$C_B = \frac{k'A}{\alpha} \cdot \frac{V_T - V_L}{V_S} \cdot \frac{b}{q} = kA \cdot \frac{V_T - V_L}{V_S} \cdot \frac{b}{q} \quad (4)$$

where $k = k'/\alpha$ is the calibration constant. A is the GC system signal peak area. b/q is the stoichiometric ratio of analyte B and the gas product Q in reaction (1). If the final total volume of the condensed phase in the reactor at the completion of the reaction V_L is very small compared to the volume of the sample vial, then the postreaction headspace volume can be approximated to the volume of the sample vial. Then Eq. (4) can be written as:

$$C_B = kA \cdot \frac{V_T - V_L}{V_S} \cdot \frac{b}{q} \approx kA \cdot \frac{V_T}{V_S} \cdot \frac{b}{q} \quad (5)$$

or simply:

$$m_B = fA \quad (6)$$

where $f = k(V_T - V_L)b/q \approx kV_T b/q$.

3. Experimental

3.1. Chemicals and black liquors

All chemicals used in the experiment were from commercial sources. A 2 mol/l sulfuric acid solution was prepared using 95–98% purity commercial

sulfuric acid (Aldrich, Milwaukee, WI, USA). A 0.1 mol/l standard carbonate solution was prepared for the calibration. All black liquor samples were collected from conventional alkaline pulping of both softwoods and hardwoods in our laboratory.

3.2. Apparatus and operation

All measurements were carried out using a HP-7694 automatic headspace sampler and a Model HP-6890 capillary gas chromatograph equipped with a thermal conductivity detector (Hewlett-Packard, now Agilent Technologies, Palo Alto, CA, USA). GC conditions were: capillary column of 30 m×0.53 mm I.D. (Model GS-Q; J&W Scientific, Folsom, CA, USA) at 30°C, carrier gas helium flow-rate of 3.1 ml/min. Headspace sampler operating conditions were: oven temperature of 60°C; 0.5 min strong shaking of the sample; vial pressurized by nitrogen and pressurization time of 0.2 min; sample-loop fill time of 0.2 min; loop equilibration time of 0.05 min; vial equilibration time of 0.5 min; and loop fill time of 1.0 min.

The sample preparation and measurement procedures were as follows: A sample vial of 21.6 ml was first sealed with a PTFE/butyl molded septum (catalog No. 73822A-20; Kimble Kontes, Vineland, NJ, USA). The sample vial was then purged by nitrogen gas at a flow-rate of 130 ml/s for 2 min to eliminate the carbon dioxide present in the air in the vial headspace before adding 0.5 ml of 2 mol/l sulfuric acid. The sealed and nitrogen-purged vial was injected 10–1000 μl of sample solution using a microsyringe and placed in the headspace sampler tray for automatic HS-GC measurements. Most industrial liquid samples, such as weak and concentrated black liquors, white liquors, and green liquors, can be directly injected into the sample vial for analysis without pretreatment. Solid samples, must be dissolved in water before analysis.

4. Results and discussion

To demonstrate the PRC-HS-GC technique, we first demonstrate the measurement of carbonate in aqueous sodium carbonate solutions through the measurements of product-gas carbon dioxide after the carbonate has been acidified using sulfuric acid. The following reaction can be used to describe the condensed phase (carbonate) conversion reaction through acidification:

$$2H^+ + CO_3^{2-} = H_2CO_3 \Rightarrow CO_2 + H_2O \quad (7)$$

The intermediate product, hydrogen carbonate acid, is unstable, and it will be converted to carbon dioxide instantly. We can then apply the developed PRC technique to determine nonvolatile species in kraft black liquors. The following reactions can be used to describe the kraft black liquor acidification reaction:

$$2H^+ + CO_3^{2-} \Rightarrow CO_2 + H_2O \quad (8a)$$

$$2H^+ + S^{2-} \Rightarrow H_2S \quad (8b)$$

$$H^+ + CH_3S^- \Rightarrow CH_3SH \quad (8c)$$

In this study, we will only demonstrate simultaneous analysis of carbonate (CO_3^{2-}) and sulfide (S^{2-}) in spent pulping liquors with thermal conductivity detection.

4.1. Temperature effect

By acidification, the carbonate can be instantly converted into carbon dioxide that has a very low solubility ($1.6 \cdot 10^{-5}$) in water at room temperature. A higher temperature can accelerate the decomposition of H_2CO_3 into carbon dioxide, as shown in reaction (7), to completely remove the carbon dioxide in the liquid phase into the vapor phase. Thus the sensitivity of determination can be improved. The vapor of an acidic medium is corrosive to the GC sampling channel. Therefore, a mild headspace temperature (60°C) was chosen in the present study. An excess amount of acid can guarantee a complete conversion of carbonate into carbon oxide. However, using a higher concentration of acid will increase the risk of the corrosion problem in the headspace sampler.

4.2. Detector linearity and constant condensed phase conversion rate tests

One key assumption adopted in the present PRC-

HS-GC is that condensed phase conversion rate is a constant at a given set of reaction conditions. It is well known that a GC thermal conductivity detector linearly responds to the mass of carbon dioxide in a sample within the detector linearity range. We can use the detector linearity to verify that a constant rate of conversion of carbonate to carbon dioxide has been achieved in Eqs. (7) and (8a). We conducted a set of experiments using an aqueous sodium carbonate solution of concentration 0.1 mol/l with different sample sizes to react with a fixed volume $V_R = 0.5$ ml of sulfuric acid (reactant R) of concentration 2 mol/l. It was found that the measured detector signal peak areas are linearly proportional to the masses of carbonate contained in the samples up to a sample size of about 100 μmol. Linear least-square fits of the data yield a linear equation of $A = 25.76 m_B$ between the detector signal, A, and carbonate mass, m_B (in μmol), with an $R^2 = 0.9998$. These results indicate that the rate of conversion from carbonate to carbon dioxide is a constant under the reaction temperature of 25°C with a ratio of sulfuric acid to carbonate of 10. The results also indicate that the detector response is linear up to a carbon dioxide mass of 100 μmol. Similar experiments were also conducted to demonstrate the constant rate of conversion of carbonate to carbon dioxide in kraft black liquors when acidified, as will be discussed in detail in the next section.

4.3. Effect of the variations in headspace gas dilution on measurement accuracy

In theory, we can calculate the effect on analysis accuracy of variations in headspace dilution between the calibration and the individual testing experiment. However, such a calculation requires knowing the volumes of the postreaction headspace in these experiments and the exact amounts of the products formed during these phase conversion reactions. Furthermore, it requires to know the amount of inert gas added into the sample vial during the individual pressurization process, an amount which is often not readily measurable.

We will use the carbonate examples to study the effect of variations in headspace gas dilution on the validity of the unity ratio of dilution assumption adopted in the present PRC-HS-GC experiments. The variations in headspace gas dilution were achieved through the variations in the initial sample size of the two reactants to alter the postreaction headspace volume $V_T - V_L$ in the reactor (sample vial). We conducted two sets of experiments using a fixed volume $V_R = 0.5$ ml of sulfuric acid (reactant R) to react with carbonate. The first set of experiments used nine samples of aqueous sodium carbonate solution containing the same amount of carbonate of 1.06 μg but with sample sizes ranging from $V_S = 100$ to 350 μl. When the same amount of carbonate is used in experiments, with the approximation of the postreaction headspace volume equal to $[V_T - (V_R + V_S)]$, the effect of headspace dilution through the variation of sample size on the measured GC signals can be calculated. For a sample vial of 21.6 ml, the GC signal variation will be less than 5% when the same size V_S varied from 100 to 1100 μl or $(V_R + V_S)$ varied from 600 to 1600 μl. The present commercial HS-GC system uses a constant pressure head during pressurization, which counterbalances the effect of headspace dilution on GC signal induced by the variation of sample size. Table 1 lists the measured GC detector signal peak areas obtained in the first set of experiments. The results show that the relative standard deviation (RSD) of the nine measurements is only 1.3%, indicating the variations in headspace dilution induced by the variations in initial total volume of the two reactants $(V_R + V_S)$ from 600 to 850 μl has a negligible effect.

The second set of experiments used 14 samples of a black liquor derived from kraft pulping of loblolly pine with TDSs of 17%. The sample sizes varied from $V_S = 20$ to 300 μl. Because the mass of carbonate is proportional to the sample size for a given liquor, it is expected that the measured GC detector signals of carbon dioxide in these 14 samples should be linearly proportional to the sample size V_S if a constant rate of conversion from carbonate to carbon dioxide is achieved. It was found that the GC detector signal peak areas A fit to a straight line of $y = 0.707x$ with respect to V_S very well with $R^2 = 0.9985$, indicating that sample-size variation within a total reactant volume $(V_S + V_R)$ range of 520–800 μl does not create significant variations in headspace dilution to affect the measurement accuracy. More importantly, the results indicate that the effect of the variations in headspace dilution due to variations in

Table 1
Effect of sample size on measurement accuracy

Sample volume (μl)	Concentration of Na_2CO_3 (mol/l)	Mass of Na_2CO_3 (μg)	Detector signal peak area (*A*)	Relative error (%)
100	0.1000	1.06	240.5	0.55
120	0.0830	1.06	241.3	0.89
140	0.0714	1.06	240.1	0.39
160	0.0625	1.06	235.2	−1.66
180	0.0556	1.06	237.5	−0.70
200	0.0500	1.06	245.6	2.69
250	0.0400	1.06	238.2	−0.41
300	0.0333	1.06	237.5	−0.70
350	0.0286	1.06	236.7	−1.04
Mean			239.2	
RSD (%)			1.3	

headspace total pressure caused by the different amounts of carbon dioxide and other gases produced in the 14 experiments also does not significantly affect the measurement accuracy. The excellent linearity relationship between detector signal, *A*, and sample size, V_S, also verifies that the constant rate of conversion of carbonate to carbon dioxide has been achieved even in a kraft black liquor that has a very complex sample matrix.

4.4. Effect of carbon dioxide in air

The carbon dioxide concentration in standard air is about 15 μmol/l. It is estimated that there are about 0.3 μmol of carbon dioxide present in the air within a 21.6-ml sample vial, which is greater than the sensitivity of the detector of 0.1 μmol and can affect measurement accuracy in solutions that have low carbonate concentrations. In particular, a very small sample size is recommended in using PRC-HS-GC. To improve measurement accuracy, it is necessary to eliminate the carbon dioxide contained in the air within a sample-vial headspace by purging the sample vials (reactors) with nitrogen before adding reactants. The vials were thoroughly purged by nitrogen using a 23-gauge needle to reduce the carbon dioxide. The results indicate that a 2-min nitrogen purge at a flow-rate of 130 ml/min is sufficient to reduce carbonate dioxide to a nondetectable level.

4.5. Measurement precision

Two sets of repeatability tests were conducted to study the precision of the present PRC-HS-GC technique. A volume of 100 μl aqueous sodium carbonate solution of concentration 0.1 mol/l was analyzed five times in the first set of experiments. A volume of 100 μl kraft black liquor from pulping of loblolly pine was also analyzed five times in the second set of experiments. The measured GC detector signal peak areas in these two sets of experiments are listed in Table 2. The results show that the RSDs are only 0.62 and 3.74% for the two sets of tests, respectively, indicating excellent repeatability and precision of the present experiments.

4.6. Effect of sample size

The effect of the variations in sample size on

Table 2
Repeatability tests of the present PRC-HS-GC method

Replica	Detector signal peak area (*A*)	
	0.1 mol/L Na_2CO_3	Kraft black liquor
1	238.9	69.8
2	242.7	64.0
3	242.2	69.3
4	240.5	70.0
5	241.3	69.7
RSD (%)	0.62	3.74

headspace gas dilution and rate of condensed phase conversion is negligible as long as the total initial reactant sample size is within 1 ml as we discussed previously. Because of the postreaction headspace volume approximation adopted in Eq. (5), there is a systematic error in using Eq. (5) that overpredicts the analyte concentration C_B. In the present study, the sample vial volume $V_T = 21.6$ ml, the initial volume of sulfuric acid (reactant R) is fixed at $V_R = 0.5$ ml, the maximum initial volume of the unknown sample $V_S = 300$ μl. The final total volume of the condensed phase at the completion of the phase conversion reaction can be approximated to $V_L \approx V_R + V_S$. Then Eq. (5) overpredicts carbonate concentration by about ≈3.7%. If the carbonate concentration is low in the sample, a larger sample volume must be used due to the detector sensitivity requirement (the sensitivity of the present detector is about 0.1 μmol of CO_2). In these applications, the postreaction headspace volume ($V_T - V_L$) can always be measured and the results should be used if it is not small compared to the volume of the sample vial. It is also recommended that the same initial volumes of the two reactants $V_R + V_S$ should be used in the calibration experiment as well as in the individual sample analysis experiment to reduce the uncertainties due to headspace gas dilution.

4.7. Experimental calibration and method validation

Calibration was conducted using aqueous sodium carbonate solutions for all the carbonate analysis conducted in this study. A set of seven sodium carbonate solution samples with a constant sample size of 100 μl was used. The concentrations of sodium carbonate in these samples were varied to achieve the desired mass of sodium carbonate. A linear calibration equation of $m_B = fA$ was obtained with an $R^2 = 0.999$ and a calibration constant $f = 3.726 \cdot 10^{-8}$ or $k = 1.725 \cdot 10^{-6}$ to be used in Eq. (5).

The present PRC-HS-GC method was validated by a standard addition method. We added various known amounts of sodium carbonate in an unknown black liquor sample of 100 μl. Then we conducted HS-GC measurements. It was found that the measured detector signal peak areas fit to a straight line very well as shown in Fig. 1. The absolute value of the intercept of 4.5 μmol on the *x*-coordinator of the fitted line is the original carbonate contained in the unknown black liquor sample; thus the carbonate concentration in the black liquor sample is 0.045 mol/l. We then calculate the carbonate concentration in the sample using Eq. (5) to be 0.044 mol/l. The difference is only 2.2%, indicating the validity of the PRC-HS-GC method.

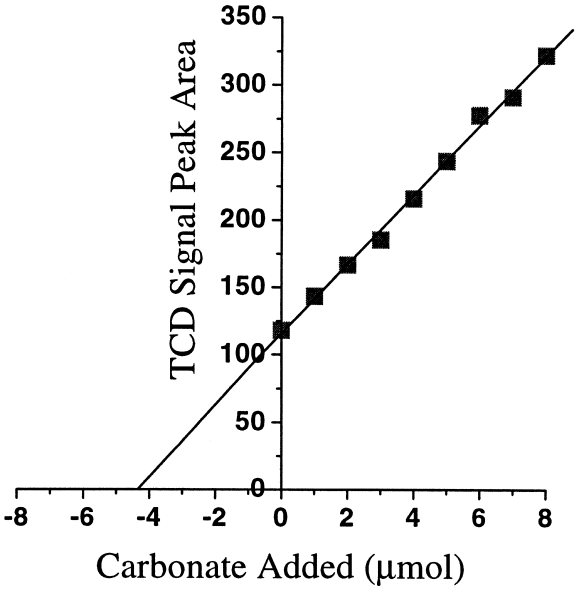

Fig. 1. Validation of measured carbonate in a black liquor sample. ■ = Experimental data; ———: $y = 115.7 + 25.645x$, $R^2 = 0.9963$. TCD = Thermal conductivity detection.

The measurements of carbonate in three different types of kraft mill samples, i.e., white, green, and black liquor samples, using the present method, were compared with two reference methods: coulometry and titrametry. A coulometric method was used by a commercial analytical laboratory (Huffman Labs., Golden, CO, USA) to measure the carbonate in the five solid black liquor samples, which had been concentrated by evaporation and then oven dried under temperature about 105°C. The carbonate in white and a green liquors was measured using a titrametric method [14] in our laboratory. The comparisons listed in Table 3 indicate that the present method is in good agreement with the two reference methods. The maximum relative difference is less than 4%.

Table 3
Comparisons of measured carbonate in kraft mill liquors by the reference methods and the present PRC-HS-GC method

Sample[a]	Carbonate carbon (%, w/w)		Relative difference (%)
	PRC-HS-GC	Coulometry	
Black liquor solid 1	1.97	2.05	−4.1
Black liquor solid 2	1.78	1.83	−2.5
Black liquor solid 3	0.98	0.95	3.0
Black liquor solid 4	1.52	1.51	0.7
Black liquor solid 5	1.61	1.53	5.0
	Sodium carbonate (g/l as Na_2O)		
	PRC-HS-GC	ABC titration	
White liquor	24.6	23.8	3.3
Green liquor	45.8	45.5	0.7

[a] The 0.4–1.1 g of solid samples were accurately weighed and dissolved in 20 ml of distilled water.

4.8. Simultaneous multiple species measurements

Sodium sulfide in black, white, and green liquors can be easily determined by titrametry. In this study, we demonstrate the versatility of PRC-HS-GC for simultaneous multiple species analysis of carbonate and sulfide through acidification reactions (8a) and (8b). A white, green, and weak black liquor were used. Carbonate and sodium sulfide concentrations in the white and green liquors were measured by both titrametry [14] and PRC-HS-GC. Because titrametry cannot be applied to black liquors for carbonate determination, carbonate was only measured by PRC-HS-GC along with sodium sulfide as shown in Table 4. Excellent agreement was obtained between the PRC-HS-GC and titrametry.

5. Conclusions

We have developed a PRC-HS-GC technique for the measurements of nonvolatile species in liquid or solid samples. The technique is demonstrated by the measurements of carbonate in aqueous sodium carbonate solutions, as well as kraft white, green, and black liquor samples. A very small amount of sulfuric acid (volume of 0.5 ml, concentration of 2 mol/l) is used to acidify the samples (volume less than 300 μl) to convert the dissolved carbonate (condensed phase) into carbon dioxide (gas) in a sample vial (reactor) that is analyzed by a thermal conductivity detector through a headspace sampler. Aqueous sodium carbonate solutions are used to calibrate the GC detector signal for carbonate determination. The technique is first validated by a standard addition approach using a kraft black liquor. The measured carbonate concentrations by the present PRC-HS-GC in five solid black liquor samples were compared with those measured using a coulometric method by commercial laboratory. Excellent agreements were obtained. Similar comparisons of the measured carbonate concentrations in

Table 4
Comparisons of measured carbonate and sodium sulfide in white, green and black liquor by the reference methods and the present PRC-HS-GC method

Sample	Sodium carbonate (g/l as Na_2O)			Sodium sulfide (g/l)		
	HS-GC	Titrametry	Relative difference (%)	HS-GC	Titrametry	Relative difference (%)
WL	24.6	23.8	3.4	42.9	41.1	2.5
GL	45.8	45.5	0.7	45.8	47.4	−3.4
BL	0.6	N/A	N/A	10.2	9.8	4.1

kraft white and green liquors were also made between the PRC-HS-GC and a titrametric method [14], with good agreement. We also conducted simultaneous analysis of carbonate and sodium sulfide in kraft white, green, and black liquor to demonstrate the versatility of the PRC-HS-GC method. It greatly simplified the analysis of carbonate in kraft black liquors. It is simple, rapid, automatic, and accurate. It can be applied to analysis of other nonvolatile species in a wide range of industrial and environmental samples.

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References

[1] H. Hachenberg, A.P. Schmidt, Gas Chromatographic Headspace Analysis, Heyden, London, 1977.
[2] B.V. Ioffe, A.G. Vitenbery, Headspace Analysis and Related Methods in Gas Chromatography, Wiley, New York, 1984.
[3] B. Kolb, L.S. Ettre, Static Headspace-Gas Chromatography – Theory and Practice, Wiley–VCH, New York, 1997.
[4] J. Drozd, J. Novak, J. Chromatogr. 165 (1979) 141.
[5] J. Namiesnik, T. Gorecki, M. Biziuk, Anal. Chim. Acta 237 (1990) 1.
[6] B. Kolb, J. Chromatogr. A 842 (1999) 163.
[7] J. Drozd, J. Novak, J. Chromatogr. 136 (1977) 27.
[8] M. Markelov, J.P. Guzowski Jr., Anal. Chim. Acta 276 (1993) 235.
[9] J.P. Romano, D.R. Salomom, in: Proceedings of the 1992 Tappi Pulping Conference, 1992, p. 303.
[10] J. Krishnagopalan, M. Hill, A.L. Fricke, Tappi J. 68 (1985) 108.
[11] D.B. Easy, M.L. Borchardt, A.A. Webb, PaPuu 67 (1985) 501.
[12] Tappi Test Method, T 699 om-87, Atlanta, GA, 1987.
[13] D.G. Davis, in: H.H. Bauer, G.D. Christlan, J.E. O'Reilly (Eds.), Instrumental Analysis, Allyn Bacon, Boston, MA, 1978, p. 102.
[14] R.G. MacDonald (Ed.), Pulp and Paper Manufacture, 2nd ed., The Pulping of Wood, Vol. 1, McGraw-Hill, New York, 1969, p. 563.