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# Surface properties of solid materials measured by modified inverse gas chromatography

Wenjuan Wang [a,b,1], Qing Hua [a,1], Yunfei Sha [a], Da Wu [a], Saijing Zheng [a,*], Baizhan Liu [a,*]

[a] *Shanghai Tobacco Group Co., Ltd, Technical Center, Shanghai 200082, China*
[b] *Shanghai Advanced Research Institute, Chinese Academy of Sciences, Shanghai 201210, China*

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ABSTRACT

A novel modified inverse gas chromatography (IGC) method has been developed to investigate the surface properties of solid materials. On the modified IGC system, the every adjusted retention time of miscellaneous probe molecules can be rapidly calculated within only one sample injection through wisely induction a capillary column and two detectors, i.e., flame ionization detector (FID) and thermal conductivity detector (TCD). In the system, the relative dead time can be acquired from FID detector while the retention time can be obtained from TCD detector simultaneously. The significant advantage of our design is that, experimental time is greatly saved compared to the traditional IGC. In addition, the new system is capable of distinguishing variety surface properties of porous materials. Two types of active carbon samples were tested, and the results showed that their thermodynamic parameters were quite different, indicating that the samples have opposite acidic/basic properties. The use of IGC would be an effective tool to evaluate the physiochemical data of solid materials.

## 1. Introduction

The fundamental understanding of interface reactions is of great importance but also remains a great challenge. Both theoretical and practical studies of the inverse gas chromatography (IGC) have been growing rapidly in the field of interface reactions between probe molecules and solid materials [1–10]. IGC, an extension of the conventional gas chromatography, is testified to be not only a powerful and valued technique to determine the surface properties and thermodynamic functions for the adsorption of various organics probes in the Henry area [6,10,11], but also a fast and reliable technique to study the surface energies of polymers, copolymers, biopolymers, fibers, coatings etc. [11–13]. This is attributed to the fact that IGC is capable of comparing the surface nature of particulate samples, which is a difficult task for conditional method [14]. The specific surface area, for example, is normally determined by using standard Brunauer–Emmett–Teller (BET) method, but this method is unavailable to measure the adsorptive capacity of adsorbent. As a result, IGC has become a widely used technique to characterize surface, in particular, the surface Lewis acidic & basic property [15,16].

However, one limit of IGC is that only single-component probes can be performed in each injection when measuring the surface properties of solid materials [17]. The normal IGC should effectively avoid the multi-components probes directly through the strong adsorbents in the packed column and thus difficult to separate. Compared with the normal IGC, the modified IGC is equipped with a capillary column to separate multi-components probes, thus, it is more flexible and simple. In this article, a novel modified IGC system was developed and the thermodynamic surface properties of active carbons were characterized. The study directly assessed the effects of various volatile molecular probes on the surface of an active carbon sample and investigated their surface properties. Both the stationary phase and the separation of probes were studied. Based on the results, the modified IGC system is capable of measuring the single-component probes as well as the multi-components ones. As to our knowledge, it has not been reported that a modified IGC system with our design is constructed to evaluate surface properties of solid materials. With our approach, the modified IGC system can be widely applied to characterizing surface properties of solid materials, such as catalysts, minerals, fibers, etc.

## 2. Modified inverse gas chromatography (IGC) method

Fig. 1 shows the schematic diagram of the modified IGC system. The necessary component of this system is a standard Agilent 6890 gas chromatograph (GC), equipped with a selected capillary

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* Corresponding authors. Tel.: +86 21 61669449; fax: +86 21 61669950.
*E-mail addresses:* zhengsj@sh.tobacco.com.cn, zhengsj1976@yahoo.com (S. Zheng), liubz@sh.tobacco.com.cn (B. Liu).

[1] Wenjuan Wang and Qing Hua contributed equally.

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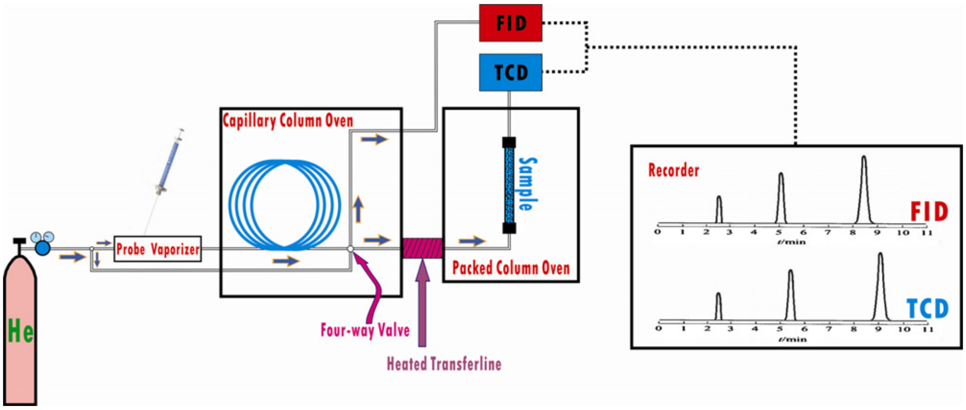

**Fig. 1.** Schematic diagram of the modified IGC system.

column and a short packed column. The channels of the four-way valve are connected, in turn, to the inlet carrier gas to enlarge the flow of carrier gas, FID detector, and the export of capillary column and the import of the packed column. Thermal conductivity detector (TCD) is connected to the packed column, thus, allowing us to analyze the adjusted retention time of probe molecules through the packed column. The micro-crosspiece is made by GERSTEL Company (Germany).

One point worth mentioning is that an external capillary column is employed in the configuration to meet the need of separation of the multi-components probes under an appropriate temperature programmed condition. The investigated samples (stationary phases) were placed in the packed column and the packed column was located in another temperature-controlled cabinet. Two respective temperature control systems allow setting different programmed temperatures on two types of column. The properties of investigated samples were determined based on the retention behavior of selected molecular probes. The adjusted retention time was measured according to the temporal difference between FID and TCD. The retention data were collected at maximum sensitivity. In the infinite dilution region injection of minor amount of adsorbents to approach zero surface coverage, the adsorption data obeyed the Henrys' law [11,18] and this system could be used for data collection over a wide temperature range. The automated injection valve was configured to inject the vapor of the mixture (appropriate mix of exultant vapor and carrier gas) into the gas flow, which transport the vapor through the column to the detectors. The multi-components probes were separated by the selected capillary column. Through a four-way valve, partial vapor that arrived at the FID detector can be used to determine the relative dead time and the rest was transferred over the investigated packed sample by carrier gas, and consequently entered into the TCD detector to determine the retention time.

## 3. Results and discussion

Our modified IGC was employed to study the surface properties of two types of active carbons [28,29]. Detailed experimental section is in the Supplementary data and detailed mathematical justification is in the Appendix. We adjusted and selected a suitable volume of sample to pack in the packed column. $CH_4$ was introduced to test the dead time [28], and the result showed that the dead time investigated by FID and TCD was exactly the same. It worth pointing out that the constant in the Formulas A4–A6 (in the Appendix) was zero. At this time, the retention time observed from the FID equaled the dead time. The BET areas of those active carbons were 898 $m^2/g$ (denoted as C-1) and 1072 $m^2/g$ (denoted as C-2), respectively. $n$-Alkane was employed to study the dispersive components of surface free energy of two active carbons (Fig. S1 in the Supplementary data). Net retention volumes ($V_N$) and relative $RT\ln(V_N)$ data are listed in Table S1–S4 (in the Supplementary data). Then, the molar free energy of adsorption of one methylene group ($\Delta G_a^{CH_2}$) adsorbed on the surface of active carbons can be calculated, and the values are −5.25 kJ/mol on C-1 and −7.10 kJ/mol on C-2. By Formula A9 (in the Appendix), the dispersive components of surface free energies ($\Delta\gamma_S^D$) of the active carbons are −154.1 $mJ/m^2$ on C-1 and −282.2 $mJ/m^2$ on C-2. The results well indicate that the lower the dispersive component of surface free energy is, the stronger adsorption ability of the active carbon is. The strong adsorption ability comes from high BET area of active carbon [28]. Of course, this reason can also well explain the difference of the molar free energy of adsorption of one methylene group ($\Delta G_a^{CH_2}$) adsorbed on the surface of active carbons.

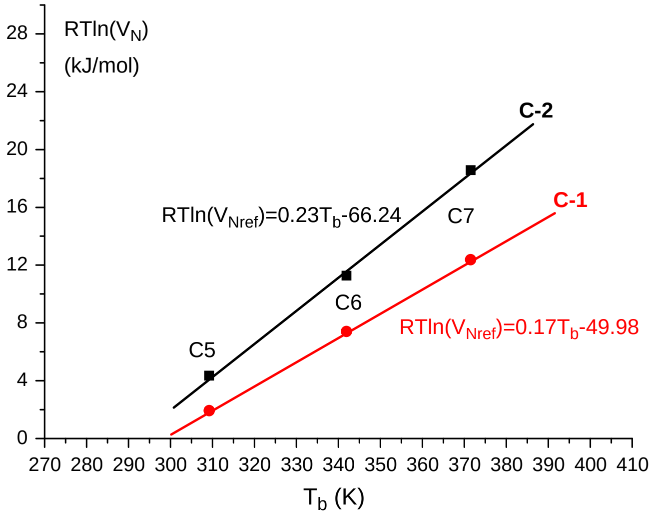

**Fig. 2.** Plots of $RT\ln V_N$ (kJ/mol) for the adsorption of $n$-alkane probe molecules on active carbons versus boiling point ($T_b$).

In order to investigate the enthalpy of the specific adsorption ($\Delta H_a^S$), the acid constant ($K_a$) and the base constant ($K_b$), the values of $RT\ln(V_{Nref})$ of polar probe molecules, which has the same boiling point as the relative $n$-alkane, should be studied [27]. $RT\ln(V_N)$ of the $n$-alkanes as a function of boiling points (taken from the NIST chemistry book in Table S5 in the Supplementary data) shows a good linear relationship, as shown in Fig. 2. The formulae of the linear relationship as follows:

$$RT\ln(V_{N_{ref}}) = 0.17T_b - 49.98 \tag{1}$$

$$RT\ln(V_{N_{ref}}) = 0.23T_b - 66.24 \tag{2}$$

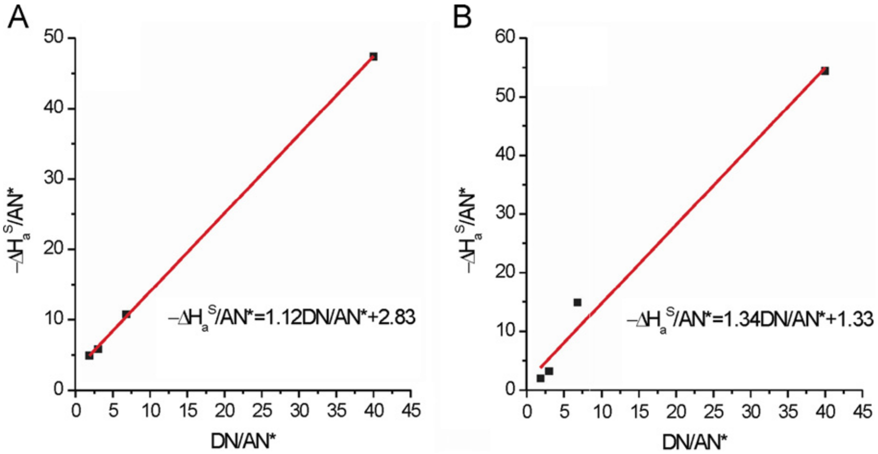

**Fig. 3.** Plots of $-\Delta H_a^S/AN^*$ versus DN/AN*, C-1 (A) and C-2 (B).

Formula 1 explains the linear relationship of RTln($V_N$) of the *n*-alkanes versus the boiling point of that on C-1 sample, and Formula 2 illustrates the linear relationship of the values of RTln($V_N$) of the *n*-alkanes versus the boiling point of that on C-2 sample. According to Formulas 1 and 2, we can calculate the RTln($V_{Nref}$) (Brookman and Sawyer method) of polar probe molecules, which has the same boiling point with the relative *n*-alkane. Then the specific component of adsorption energy ($\Delta G_a^S$) of the polar probe molecule (Fig. S2 and S3 in the Supplementary data) can be determined by Formula A11 (in the Appendix), and the detailed values of those are listed in Table S6–S9 (in the Supplementary data), Reference to Formula A12 (in the Appendix), the specific components of enthalpy of adsorption ($\Delta H_a^S$) can be easily got as shown in Table S9.

When the specific components of enthalpy of adsorption ($\Delta H_a^S$) are available and the donor (DN) and acceptor (AN*) numbers of the polar probe molecules are obtained (shown in Table S5 in the Supplementary data), the empirical relationship given by Formula A13 (in the Appendix) can be used to establish the acid–base parameter of the surface of the investigated active carbon samples. Fig. 3 shows the plots of $-\Delta H_a^S/AN^*$ versus DN/AN*. From the plots of C-1 sample (Fig. 3A), a $K_a$ value of 1.12 and a $K_b$ value of 2.83 were found, indicating a basic surface. At the same time, from the plots of C-2 sample (Fig. 3B), the value of $K_a$ is 1.34 while $K_b$ is 1.33, indicating a neutral surface.

## 4. Conclusions

In conclusion, we have developed a novel and rapid method to measure surface properties of solid materials by modified IGC. Compared with the normal IGC method, a selected capillary column is employed to separate the multi-components probes, so that, different retention time of the diverse probes can be determined during only one injection. Meanwhile, two detectors, FID and TCD, are equipped on a GC. Relative dead time can be acquired from FID detector and retention time can be obtained from TCD detector simultaneously, therefore, the adjusted retention time can be easily calculated. In addition, the surface properties of two types of active carbons were studied on the modified IGC. This modified IGC measurement provides an easy and quick method to investigate the physiochemical data of solid materials.

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## Appendix. Mathematical justification

The evaluation method of modified IGC to determine the thermodynamic parameters of targeted samples in this article was based on the analysis of adsorption of gaseous probes on the surface of investigated adsorbents. The surface properties of the aimed samples were determined mainly by the adjusted retention time using the modified IGC system to accurate the net retention volume ($V_N$) of molecular probes. In the experiment, the magnitude of interaction among each probe vapor and investigated sample reflects in the value of net retention volume ($V_N$). The first step was to determine the net retention volume which was the volume of carrier gas necessary to elute an adsorbed probe from the column under the special conditions of temperature and pressure. The net retention volume of volatile standard is directly related to its thermodynamic interaction with the surface. It is defined as the volume of carrier gas required to sweep out an adsorbed probe from the chromatographic column. The net retention volume is calculated by the following formula [18–23]:

$$V_N = t_R' \times F \times \frac{3}{2} \times \frac{(P_i/P_o)^2-1}{(P_i/P_o)^3-1} \tag{A1}$$

where $V_N$ is the net retention volume, $t_R{}'$ is the adjusted retention time, $F$ is the carrier gas flow rate (mL/min), $P_i$ is the packed column inlet pressure, and $P_o$ is the packed column outlet pressure.

In this article, a fast method to calculate the adjusted retention time has been developed. According to Fig. 1, the retention time of FID and TCD can be calculated as follows:

$$t_{R,TCD} = t_{R,CC} + t_R' + t_{M,TCD} \tag{A2}$$

$$t_{R,FID} = t_{R,CC} + t_{M,FID} \tag{A3}$$

where $t_{R,TCD}$ is the retention time acquired from TCD, and $t_{R,FID}$ is the retention time acquired from FID. $t_{R,CC}$ is the retention time before the four-way valve, the valve of which is controlled by the capillary column. $t_{M,TCD}$ is the dead time spent between four-way valve and TCD, and $t_{M,FID}$ is the dead time spent between four-way valve and FID.

Generally, the difference of $t_{M,TCD}$ and $t_{M,FID}$ is a constant (denoted as $C$, $t_{M,TCD} - t_{M,FID} = C$). The adjusted retention time (Formula A2–Formula A3) can be expressed as:

$$t_R' = t_{R,TCD} - t_{R,FID} - C \tag{A4}$$

The classical adjusted retention time expressed as follows:

$$t_R' = t_{R,TCD} - t_{M,TCD} \tag{A5}$$

Compared with the Formulas A4 and A5, the retention time acquired from FID detector is relative with the dead time of the sample:

$$t_{M,TCD} = t_{R,FID} + C \tag{A6}$$

In order to determine the free energy of adsorption for different probes, the net retention volume $V_N$ has to be measured on different probes. According to the theory of the gas chromatography, the probe vapors are adsorbed and desorbed in and through the chromatographic column. The molar free energy of adsorption ($\Delta G_a$) of a probe on the packing column can be estimated with the following formula [23]:

$$-\Delta G_a = RTInV_N + K \tag{A7}$$

where $R$ is the ideal gas constant, $T$ is the column temperature, and $K$ is a constant.

Only dispersive (Lifshitz–van der Waals) interactions occur between non-polar probes and the solid surface. The molar free energy of adsorption of one methylene group ($\Delta G_a^{CH_2}$) can be calculated as follows [23,24]:

$$-\Delta G_a^{CH_2} = -(\Delta G_a^{C_{n+1}H_{2n+4}} - \Delta G_a^{C_nH_{2n+2}}) = -RT\frac{\ln V_N^{C_nH_{2n+2}}}{\ln V_N^{C_{n+1}H_{2n+4}}} \tag{A8}$$

where $V_N^{C_nH_{2n+2}}$ is the net retention volume of $n$-$C_nH_{2n+2}$, and $V_N^{C_{n+1}H_{2n+4}}$ is the net retention volume of $n$-$C_{n+1}H_{2n+4}$.

According to Dorris and Gray method, the dispersive component of surface free energy ($\Delta\gamma_S^D$) of the investigated samples can be estimated with the following formula [23]:

$$\Delta\gamma_S^D = -\frac{(\Delta G_a^{CH_2})^2}{4N^2(a_{CH_2})^2\gamma_{CH_2}} \tag{A9}$$

where $a_{CH_2}$ is the surface area of a methylene group, the value of that is assumed to be equal to 6 Å$^2$ in this article [23]. $\gamma_{CH_2}$ is the surface energy of the polyethylene-type polymers with a finite molecular weight (mJ/m$^2$). The value of $\gamma_{CH_2}$ is calculated according to the following formula [23]:

$$\gamma_{CH_2} = 35.6 + 0.058 \times (293 - T) \tag{A10}$$

Acidity and basicity of solid surface are concluded from the behavior of polar compounds being injected into the chromatographic column filled with investigated sample by IGC method. Both dispersive and specific interactions occur between polar probes and the solid surface. In order to investigate the specific parameters, the specific component of adsorption energy ($\Delta G_a^S$) should be determined firstly. $\Delta G_a^S$ can be obtained by calculating the difference of the adsorption energy of polar probes ($\Delta G_a$) and the dispersive component of adsorption energy ($\Delta G_a^D$) [23].

$$\Delta G_a^S = \Delta G_a - \Delta G_a^D = -RT\ln\frac{V_{N_{polar}}}{V_{N_{ref}}} \tag{A11}$$

$\Delta G_a^D$ is determined by adsorption energy of hypothetical alkane having the same selected property as polar probe, such as $a\gamma_L^D$ value in Schultz and Lavielle method, boiling point ($T_b$) in Brookman and Sawyer method and vapor pressure ($\ln P_o$) in Papirer method. $V_{N_{polar}}$ and $V_{N_{ref}}$ are the net retention volume of polar probe and selected hypothetical alkane, respectively.

Specific component of enthalpy of adsorption ($\Delta H_a^S$) and entropy of adsorption ($\Delta S_a^S$) may be calculated from the temperature dependence of the specific component of free energy of adsorption ($\Delta G_a^S$) at given coverage. In the experiment, plots of $\Delta G_a^S/T$ versus $1/T$ at constant coverage get a straight line. And the slope gradient is $\Delta H_a^S$ and the intercept is $-\Delta S_a^S$ [25,26]. The accurate formula is as follows:

$$\Delta G_a^S = \Delta H_a^S - T\Delta S_a^S \Leftrightarrow \frac{\Delta G_a^S}{T} = \frac{1}{T}\Delta H_a^S - \Delta S_a^S \tag{A12}$$

Specific component of enthalpy of adsorption ($\Delta H_a^S$) of polar probe is related to acceptor and donor numbers describing the electron acceptor (AN$^*$) and electron donor (DN) properties of the probe molecular [24,27].

$$-\Delta H_a^S = DNK_a + AN^*K_b \Leftrightarrow -\frac{\Delta H_a^S}{AN^*} = \frac{DN}{AN^*}K_a + K_b \tag{A13}$$

Parameters $K_a$ and $K_b$ describe the ability of the investigated sample to act as electron acceptor and donor, respectively. They are taken as the slope and intercept, respectively, of the trend line derived from the plot of $-\Delta H/AN^*$ versus $DN/AN^*$ at constant coverage, the slope of which is $K_a$ and the intercept is $K_b$.

## Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2013.03.040.

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