



ANALYTICAL SERIES

Inverse Gas Chromatography Characterization of Coatings

by Ewa Langer and Grażyna Kamińska-Bach

Institute for Engineering of Polymer Materials and Dyes

Gas chromatography (GC) is a valuable analytical method for evaluating volatile organic compounds. Inverse gas chromatography (IGC), on the other hand, is a method used in evaluating the physical and chemical properties of organic and inorganic nonvolatile compounds such as polymers, pigments, fillers, catalysts, or active solids.

INTRODUCTION

Chromatography has been known since the beginning of the 20th Century and is used to determine the thermodynamic properties of solids.¹ The method is a product of the research performed by the Russian botanist M.S. Cwiet, who studied the coloring compounds of leaves, and was the first to separate them by means of a chromatographic process. Today, chromatography is one of the most widely used instrumental methods in analytical chemistry and the most important one in organic compound analysis.

Inverse gas chromatography (IGC) was introduced as a test method in 1967. It is identical to conventional gas chromatography in its workings, and as such does not require any special apparatus.² Kiselev is believed to have established inverse gas chromatography as a separate research method. Smidsrod and Guillet³ have also played a significant role in the development of the methodological and theoretical concepts in this area.

The objective of inverse gas chromatography is the evaluation of the interactions between volatile test sub-

stances and nonvolatile stationary phase substances, hence the name “inverse.” The physical and chemical properties of nonvolatile substances are assessed through an analysis of the retention volumes of volatile test substances with pre-defined properties. Polymers, pigments, fillers, active carbons, or catalysts² can be used as stationary phases.

MEASUREMENT PRINCIPLES

Determining the properties of a substance by means of inverse gas chromatography is performed by placing the material being assessed (polymer, pigment, filler, catalyst) in a chromatographic column, one end of which is connected to an injector and the other to a detector (a flame ionization detector is the one most commonly used). Afterwards, selected test substances are injected into the column, which, after reacting with a carrier gas (nitrogen, argon, helium) having a specified flow rate, causes them to elute. The final stage is the detection of the substances eluted from the column to determine the desired retention values. *Figure 1* provides a schematic overview of the typical layout of a gas chromatograph.⁴

Chromatographic Columns

The way in which chromatographic column is filled depends on the type of compound tested. Pigments and fillers can be packed into the column directly. However, due to the high pres-

sure values present at the entrance to the column, this method is rarely used. They are most commonly mixed with an inert substance (i.e., neutral, having no impact on intermolecular interactions).

Columns for testing polymers and resins, whether or not they have been crosslinked, can be prepared in two ways. The first method involves placing the tested polymer on an inert carrier. Once the right volume of a tested stationary phase (polymer) is weighed, it is then dissolved in a specified volume of volatile solvent. The tested substance is subsequently poured onto the inert substance which had been heated earlier to a temperature of 200°C for approx. two hours and by gentle stirring until the solvent is vaporized. The carrier, which is then covered by a layer of the analyzed substance, is placed inside the column. The other method involves filling the column with only the tested, finely ground polymer having a specified thickness, for the sake of achieving optimum pressure at the entrance to the column and optimal retention time for the tested substances.

Empty columns and laboratory glass used during the preparation of the column should be rinsed with an organic silane compound, such as dimethylchlorosilane (DMCS), to eliminate any potential reactions between the glass and the test substances being introduced inside. Ready-for-use columns must be conditioned, i.e., heated before testing can proceed.

Inert Substances—Carriers

Currently, the majority of carriers used are of the diatomite type. The varieties used most commonly are chromosorbs identified by letters, such as W, P, or G. The surface of the carrier may be modified but does not need to be. The modification involves rinsing it with acid, which is identified by the letters AQ (acid washed) or rinsing it with acid and subsequently subjecting it to silanization. The acid removes iron as well as other metals from the surface of the carrier, which may lead to the formation of active foci where present. Silanization serves to replace hydroxyl groups, present on the carrier's surface, with methylsilyl groups. Silanization is performed by means of dimethylchlorosilane (AW DMCS) or hexamethyldisilazane (AW HMDS).¹

Test Compounds

The test compounds injected into the column are low organic solvents with identified properties. The measured retention parameters (retention values) of test compounds depend on the type and power of intermolecular interactions (affinity) between each one of them and the tested solid compound.⁵

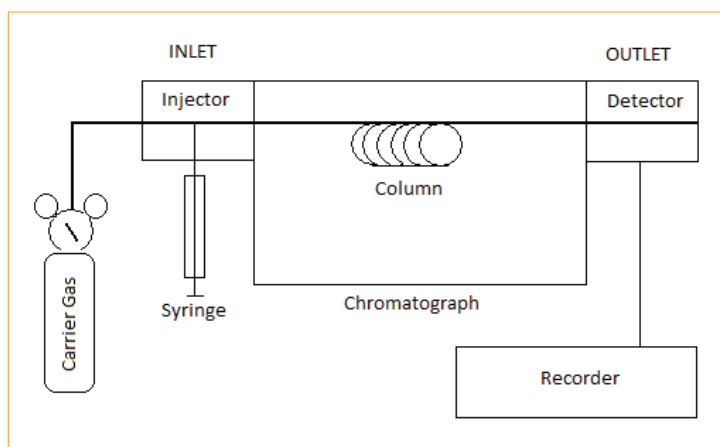


Figure 1—Schematic illustration of a typical gas chromatograph.

The test substance is chosen in such a way as to ensure that its interactions with the compounds placed inside the column reflect its specific properties: surface size, acidity or basicity of active foci on the surface, as well as polarity and solubility parameters. Table 1 presents sample solvents used in the IGC method, including their properties.

Retention Parameters Used in IGC

The chromatographic separation effect is demonstrated by an elution curve (chromatogram), which illustrates the dependency of the analytic signal with regard to the retention time or retention volume. Retention time is the time during which a test substance is present in the column.⁷

Table 1—Solvents Used in the Inverse Gas Chromatography Method⁶

Lp.	Name	M	T _c , K	p _c , atm	ρ, g/cm ³	δ, (J/cm ³) ^{1/2}
1	Hexane	86	508	29.5	0.65	14.9
2	Heptane	100	540	26.8	0.68	15.3
3	Octane	114	569.4	24.6	0.70	15.9
4	Chloroform	119.4	533.9	54.9	0.79	19.0
5	Carbon tetrachloride	153.8	556.2	45	1.60	17.8
6	Cyclohexane	84	554.2	24.6	0.78	16.8
7	Benzene	78	561.8	40	0.88	18.6
8	Ethyl benzene	106	617	29.6	0.87	17.8
9	Methanol	32	513	78.7	0.79	29.7
10	Ethanol	46	516	63.1	0.79	26.6
11	Butanol	74	560	48.4	0.81	23.1
12	Acetone	58	538	47.0	0.79	20.0
13	Ethyl ether	74	467.0	35.5	0.71	15.7

Key: M = molecular mass, T_c = critical temperature, p_c = critical pressure, ρ = density, δ = solubility parameter

t'_R —reduced retention time [s],

$$t'_R = t_R - t_0 \quad (1)$$

t_R —total retention time (from introduction of the solute to the chromatographic column until its peak maximum is reached in the chromatogram) [s],

t_0 —dead time—retention time for a gas which does not get sorbed [s],

V_N —absolute retention volume [cm³],

$$V_N = t'_R \cdot F_0 \cdot j \quad (2)$$

F_0 —volumetric carrier gas flow rate [cm³/s],

J —correction coefficient adjusting the equation by the value of gas pressure present in the column [dimensionless],

$$j = \frac{3 \left(\frac{P_1}{P_0} \right)^2 - 1}{2 \left(\frac{P_1}{P_0} \right)^3 - 1} \quad (3)$$

p_0 —carrier gas pressure at column exit [atm],

p_1 —carrier gas pressure at column entrance [atm],

V_g —specific retention volume—retention volume in relation to 1 g of liquid phase or 1 g of adsorbent at a temperature of 0°C [cm³/g],

$$V_g = \frac{V_N \cdot 273.15}{w_L \cdot T} \quad (4)$$

w_L —total stationary phase mass in the column [g],

T —column's operating temperature [K].

I —Kováts retention indices [dimensionless],

introduced in 1958 by the Hungarian researcher Kováts⁸ living in Austria, are a form of retention of relative values. Their values are calculated using the following equation:

$$I_x = 100 \frac{\log t'_{R_x} - \log t'_{R_n}}{\log t'_{R(n+1)} - \log t'_{R_n}} + 100n$$

$$\text{dla } t'_{R_n} < t'_{R_x} < t'_{R(n+1)} \quad (5)$$

t'_{R_x} —reduced retention time [s],

n —number of carbon atoms in an n -alkane [dimensionless],

t'_{R_n} —reduced retention time in an n -alkane [s].

Within this system, the retention indices of n -paraffins are pre-specified (their value amounts to $100n$) and are a type of scale used for calculating retention indices of other compounds.

APPLICATION OF INVERSE GAS CHROMATOGRAPHY

One of the most important areas where inverse gas chromatography is used is in evaluating adsorbents and inorganic catalysts, primarily in the determination of their specific surface, adsorption isotherms, adsorption temperature, as well as other thermodynamic functions relating to the adsorption of volatile compounds on solids.

Other applications chiefly involve the physical and chemical characterization of polymers.⁹ Some of the main uses of inverse gas chromatography include:

- Polymer identification
- Determination of the average molecular mass
- Determination of the phase transition temperatures
- Determination of the kinetics of a chemical reaction between a polymer and a reactive gas
- Determination of intermolecular interaction thermodynamics between the standard and polymer as well as acidic and base characteristics of the polymer being evaluated
- Determination of the solubility parameters of solids

Polymer Identification

Use of the inverse gas chromatography method in order to identify polymers has been demonstrated by Berezkin et al.⁹ They discovered that the method can be used to identify stationary phase compound groups. Identification is based on the principle stating that the retention values of standards with a different chemical character for a given solid substance depend on the substance's chemical structure. For the purpose of identifying the compounds, special parameters are also used, i.e., relative coefficients determining the interaction between standard compounds and the I_g stationary phase:

$$I_g = 100 \log \frac{V_R^0}{V_{RP}^0} \quad (6)$$

where V_R^0 and V_{RP}^0 are retention values of the standard and the n -paraffin hydrocarbon with a hypothetical molecular mass equal to the molecular mass of the standard.

Determining the Molecular Mass of Oligomers

Various molecular mass values of polymers lead to changes in their properties. Measurement of the molecular mass of polymers is normally based on the properties of solutions of the

substances being analyzed (e.g., cryoscopy, the viscosity method). Since the main principles behind gas chromatography theory are identical to those used in other methods, which are based on solution properties, inverse gas chromatography can also be used in calculating molecular weight.¹⁰

Determination of the Phase Transition Temperatures

Inverse gas chromatography can be used to characterize phase transitions in solids. When analyzing adsorption on the surface of solids, the natural logarithm diagram of the retention volume in relation to inverse critical temperature presents itself as a straight line. Adsorption heat may be determined based on the diagram by means of Henry's law. Amorphous materials heated at their vitrification temperature normally produce a z-shaped curve. An example diagram is presented in Figure 2.

In area I ($T < T_g$), the proposed sample retention mechanism is surface adsorption. The first deviation of the straight line structure is caused by the first stage of glass transition. The glass and flexible states co-exist in the transformation area (Area II), where the retention mechanism is a combination of surface adsorption and physical sorption. The retention volume increases in this area. This lasts until the end of area II, whereas the retention volume decreases with the rise in temperature in area III.

The peak maximum on the curve occurs at the temperature at which the polymer's crystalline phase disappears, which is referred to as flow temperature. In the case of crystalline polymers, it is known as the melting temperature.

Determination of the Kinetics of a Chemical Reaction Between a Polymer and a Gas

The IGC method can also be used to determine the kinetics of a chemical reaction, where the reaction taking place in a chromatographic column between the stationary phase and the carrier gas is evaluated. The retention volumes of selected solutes enable a calculation of the degree of over-reaction in the system to be calculated. The following dependencies are used in the calculations:

$$C_i = f(V_g) \quad (7)$$

C_i —concentration of one of the components in the reaction mixture [mol/dm³].

The advantage of this method is that a thin layer of the stationary phase makes it possible to maintain stable reaction conditions during its course and trace consumption of the tested substances.⁹

Determining the Acidic and Base Characteristics of a Tested Polymer

The interactions between the polymer being tested and the test substance can be divided into dispersive and specific. Their corresponding determiners are the dispersion (γ_s^d) and specific (γ_s^s) components of the free surface energy of the adsorbent (γ_s):

$$\gamma_s = \gamma_s^d + \gamma_s^s \quad (8)$$

The test substances' polar adsorption free energy is a total of the free adsorption energy of dispersion interactions and specific interactions:

$$\Delta G^0 = \Delta G^d + \Delta G^s \quad (9)$$

whereas ΔG^0 is determined based on the V_n absolute retention volume of the polar substance:

$$\Delta G^0 = -RT \ln V_n \quad (10)$$

If the test substances are n-alkanes (non-polar substances), then their ΔG^0 free sorption energy is connected only to dispersive interactions and changes linearly with the number of atoms in the alkane, which makes it possible to determine the methylene group adsorption component:

$$\Delta G_{CH_2} = -RT \ln(V_{n_n} / V_{n_{(n+1)}}) \quad (11)$$

where: $V_{n_n}, V_{n_{(n+1)}}$ = absolute retention volumes of alkanes with a carbon atom number of n and (n + 1) respectively.

Based on the ΔG_s temperature dependency, the ΔH^s specific interaction enthalpy can be determined:

$$\Delta H^s = -T^2 \cdot \delta(\Delta G^s / T) / \delta T \quad (12)$$

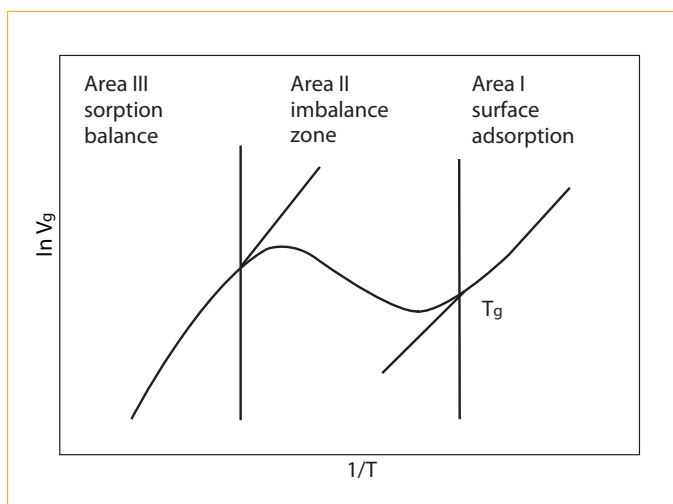


Figure 2—Ln retention volume dependency in relation to inverse temperature for an amorphous material in the area of its vitrification temperature.

According to the concept by Gutman, Lewis acids are characterized by the AN acceptor value and Lewis bases by the DN donor number. The interaction enthalpy between acid and base foci is equal to the product of both the numbers:

$$-\Delta H = AN \cdot DN \quad (13)$$

According to the proposal put forward by Papirer, et al, specific interaction enthalpy between the solvent and the tested substance can be expressed by means of the following formula:

$$-\Delta H^s = K_A \cdot DN + K_D \cdot AN \quad (14)$$

where:

K_A =a parameter characterizing the acidic impact of the tested substance; and

K_D =a parameter characterizing the base impact of the tested substance.

By determining the ΔH^s value of a series of test substances of an acidic, base, and amphoteric nature, the K_A and K_D parameters of the tested substance can be calculated, thus allowing for the determination of its capacity for acidic and base interactions.

Determination of the Solubility Parameters of Solids

The surface properties define such parameters of solids as: adhesion, wettability, abrasion, vulnerability to coloring and corrosion, as well as biological compatibility. Acidic and base functional centers located on the surface lead to a growth in the intermolecular interactions with other substances such as solvents, plastifiers, other polymers, binding materials, or fillers.⁵

The interactions between pigment molecules and membrane forming resins used in coating products have a significant impact on the properties of the coatings obtained. These interactions normally take the form of secondary intermolecular bindings, which appear between the polymer chain and groups located on the surface of, for instance, the pigment.

In the coatings industry, a group of indicators which are of key importance in characterizing raw materials are their solubility parameters.¹¹ They help define areas of mutual solubility and compatibility of components, which leads to the creation of a stable coating. An assessment criterion defining the compatibility of two components is the so-called compatibility parameter (β), which is linked to the solubility parameters of the components, according to the equation:

$$\beta = (\delta_1 - \delta_2)^2 \quad (15)$$

where:

δ_1 =total solubility parameter of one component,

δ_2 =total solubility parameter of the second component,

If $\beta \leq 0.7$ -1 MJ/m³, then total solubility of the components forming part of the composition is observed; if $\beta = 1$ -3 MJ/m³, then partial (segmental) solubility is observed, and if $\beta \geq 3$ MJ/m³, then no natural solubility occurs.¹² The greater the value of parameter β , the more the polymer pair is incompatible.

The values of solubility parameters are calculated theoretically for low molecular compounds; however, they must be experimentally determined for such compounds as polymers, fillers, or pigments. Attempts have been made to calculate the solubility parameter values for polymers,¹³ but, the calculation error was too great and inadequate knowledge of the structure of the compound proved to be an obstacle as well. On the other hand, determining solubility characteristics necessitates the use of large amounts of solvents or more refined raw materials in popular experimental methods such as those based on the values of solubility, the degree of swelling, those based on the determination of polymer softening temperature, or solution intrinsic viscosity measurements. These methods are not very precise either. Inverse gas chromatography, which is receiving increasingly more attention, is an alternative to the other methods used to determine solubility parameters.

The total solubility parameter of a tested substance can be determined by use of the following equation:

$$\frac{\delta_1^2}{RT} - \frac{\chi_{1,2}^\infty}{V_1^0} = \frac{2\delta_2}{RT} \cdot \delta_1 - \frac{\delta_2^2}{RT} \quad (16)$$

where:

δ_1 =solubility parameter of the standard substance (solvent) [(J/dm³)^{1/2}],

δ_2 =solubility parameter of the tested substance [(J/dm³)^{1/2}],

R=gas constant,

T=column's operating temperature [K],

χ_s^∞ =entropic component of the Flory-Huggins parameter [dimensionless],

$\chi_{1,2}^\infty$ =Flory-Huggins parameter, parameter identifying the interaction between the standard substance and stationary phase [dimensionless],

V_1^0 =molar volume of the standard substance in the column's operating temperature [dm³/mol].

Flory-Huggins parameter is a parameter defining the interaction between the standard substance

and the stationary phase, necessary for the determination of the solubility parameter, which can be calculated by means of the following equation:

$$\chi_{1,2}^{\infty} = \ln \Omega_1^{\infty} + \ln \left(\frac{\rho_1}{\rho_2} \right) - 1 \quad (17)$$

where:

Ω_1^{∞} = indicator of the activity of the substance being sorbed at an infinite degree of solubility [dimensionless],

ρ_1 = density of the stationary phase [g/dm³],

ρ_2 = density of the standard substance [g/dm³],

V_2^0 = molar volume of the stationary phase [dm³/mol].

The **activity coefficient of the sorbed substance**

Ω_1^{∞} is calculated according to the following equation:

$$\ln \Omega_1^{\infty} = \ln \left[\frac{273.15 \cdot R}{P_1^0 \cdot V_g \cdot M_1} \right] - \frac{P_1^0}{RT} (B_{11} - V_1^0) \quad (18)$$

where:

P_1^0 = vapor pressure of the solute [atm],

M_1 = molecular mass of the standard substance [g/mol],

B_{11} = second virial coefficient of the standard substance at column operating temperature [dm³/mol],

V_g = specific retention volume at a given temperature [cm³/g].

CONCLUSION

This article describes the inverse gas chromatography method as a valuable research tool for evaluating both organic and inorganic compounds. The method revolves around the evaluation of the interactions between a test substance and a solid constituting the stationary phase in a chromatograph. The retention values of the test substance,

which are defined during measurement, reflect its intermolecular interactions with the stationary phase in the column. The obtained figures are then used to calculate the thermodynamic functions of various compounds such as polymers, pigments, fillers, catalysts, or adsorbents. Furthermore, in polymer chemistry, the figures can be used to identify the compounds themselves or to determine their average molecular mass, phase transition temperature, chemical reaction kinetics, or their acid and base characteristics.

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AUTHORS

Ewa Langer and **Grażyna Kamińska-Bach**,
Institute for Engineering of Polymer Materials and
Dyes, Poland, 87-100 Toruń, ul. M. Skłodowskiej-Curie
55, e-mail: e.langer@impib.pl.