A way to better analyse surface properties of planar substrates as coated metals, polymers and adhesives

Application note | April 2020

Field of applications

Plate shaped materials | Steel & Aluminum | Coating | Metallic sheets

Executive summary

Planar surfaces are often treated or coated (e.g. with epoxy, organics, adhesives, metallic coating…) to provide certain properties as corrosion resistance, friction or stickiness. In many cases contact angle measurements or application tests are sufficient – but quite a few applications are more tricky. Surfaces can be rough or porous, liquids may penetrate as in adhesive films or adsorption of special gases are of interest. In all those cases, existing methods are quite unsatisfactory and a chemical or microscopic analysis does not reveal the surface properties. Subsequently, optimization of the coating or the film is not an easy task and continuing blind-folded endless trials is ineffective and expensive.

How to go further in the characterization and understanding of surface properties of planar surfaces? How to support the product development in a more efficient approach?

Inverse Gas Chromatography is an established analytical technique for very sensitive surface characterizations. In this context, **Adscientis has developed and patented an innovative device to perform in-situ studies of plates or foils** in a quantitative and reproducible way. This device allows the analysis of planar materials like glass, steel, aluminum, metals, polymers and even adhesive films. Currently, IGC is the only method known to provide such deep insight of surface properties for planar-type materials.
Based on the example of coated metallic plates, this application note focusses on the surface properties obtained by the method, such as surface energies, polarities, nanoroughness, specific surface area and surface heterogeneity. Knowing all these parameters supports the product developers quest for improved and innovative products.

Objectives

The purpose here is to demonstrate the ability of the Inverse Gas Chromatography (IGC) to characterize and assess the surface of two stainless steel metallic plates. IGC analysis is a powerful and sensitive technique to better understand the surface in terms of surface energy, presence of an organic coating and surface heterogeneity. In this application note, two plate shaped materials, Sheet 1 and Sheet 2, are used as examples to test the performance of IGC for the analysis of planar materials.

Principle

The investigated plate (10 cm x 10 cm) is mounted onto a special device dedicated to planar surface materials [1] (**Figure 1**). This device includes two supporting metallic plates, one being used as a mounting plate for a teflon plate with a chromatographic path and the other as a tightening backplate. The role of the teflon plate with a chromatographic path is to force the carrier gas to flow between the chromatographic plate and the investigated sheet. The exposed surface area is 28.8 cm^2 due to the design of the chromatographic path.

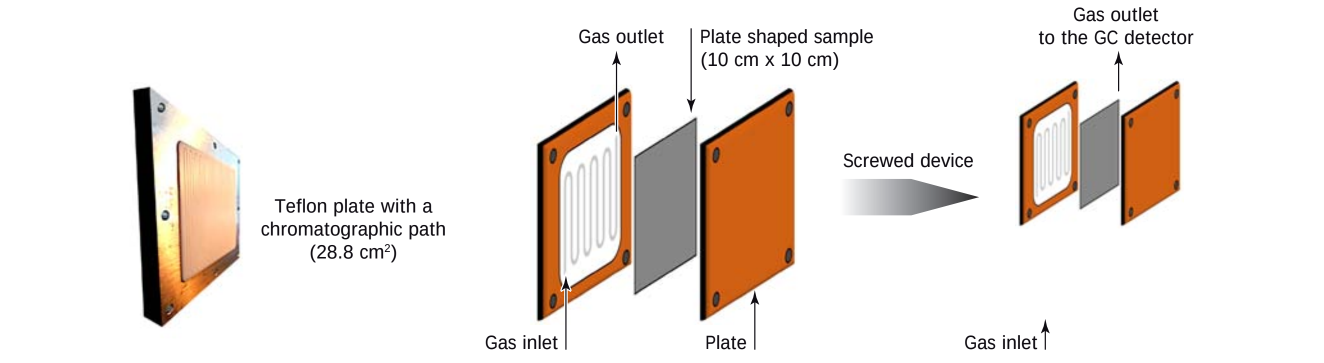

Figure 1 - Picture (left) and schematic (right) of Adscientis plate shaped analysis device

The planar surface device can be mounted directly inside the GC oven allowing thereby any operating temperature. The inlet and outlet of the chromatographic path is connected directly to the injector and to the detector of the GC. Thereafter, the standard measurement procedure in IGC is carried on. This device makes it possible to perform IGC measurements on sheet type materials to acquire the classical surface characteristics:

- the surface energy (γ_s^d)
- the surface nanoroughness (IM & relative morphological index (RIM))
- the surface cleanliness (coating and/or organics)
- the surface acid-base character (Ka & Kb)
- the specific surface area (S_{BET}, C_{BET})
- the surface energetic heterogeneity (adsorption energy distribution function AEDF)

For a better understanding of the IGC technique and the different methods, please refer to Adscientis technical sheet on "IGC-ID" [2] and "IGC-FC" [3].

Examples

General scope:

Surface coating and/or cleanliness are crucial parameters when dealing with plate shaped materials like glass, steel, aluminum, metals, polymers, polymeric films. Understanding the surface of the plate, especially when coated with an inorganic or organic film, is a key parameter to optimize surface specific properties as friction, adsorption, adhesion or metal-metal contacts. Therefore, analyzing and characterizing the surface of these plates by Inverse Gas Chromatography can give in-depth information of the surface aspect and properties. In this application note, we take the example of two unknown stainless-steel sheets for which we fully characterize their surface with IGC, basically looking at the surface energy, the existence of a uniformly distributed coating or not, and the surface energetic heterogeneity.

Results:

Two stainless steel plates (Sheet 1 and Sheet 2) were characterized by IGC. The 10 cm x 10 cm plates were mounted into Adscientis surface planar device and fitted in the GC oven. Before any measurement, the samples are outgassed during one night at 25°C under a He gas stream. All the measurements were performed at 25°C. The samples were characterized following two methods: IGC at Infinite Dilution (DI) and at Finite Concentration (FC). For more details about these two methods, please refer to Adscientis technical sheet on "IGC-ID" [2] and "IGC-FC" [3].

Table 1 - Surface parameters determined for the metallic sheets at 25°C

	Sheet 1	Sheet 2
Surface energy		
γ_s^d [mJ/m^2]	34.4 ± 0.8	31.2 ± 0.2
Surface nanoroughness		
IM(Isooctane)	0.284 ± 0.007	0.452 ± 0.014
IM(Cyclooctane)	0.805 ± 0.005	0.774 ± 0.014
RIM	2.836 ± 0.094	1.713 ± 0.086
Surface energy		
Acetonitrile [kJ/mol]	11.5 ± 0.2	11.8 ± 0.1
Chloroform [kJ/mol]	9.8 ± 0.2	8.3 ± 0.1
Acetone [kJ/mol]	6.1 ± 0.4	6.2 ± 0.1
Me-Acetate [kJ/mol]	5.4 ± 0.2	5.5 ± 0.1
Ether [kJ/mol]	3.3 ± 0.3	1.8 ± 0.2
THF [kJ/mol]	5.5 ± 0.2	4.9 ± 0.1
Benzene [kJ/mol]	4.9 ± 0.2	4.8 ± 0.1
∑ISP [kJ/mol]	46.5 ± 1.6	43.3 ± 0.8
Acid-Base		
Ka	6.7	0
Kb	48.6	52.6

At Infinite Dilution (DI), around 15 molecular probes are injected to determine the dispersive component of the surface energy (γ_s^d), the nanoroughness or the surface cleanliness (IM & RIM) and the acid base character (Ka & Kb). Table 1 summarizes the determined surface parameters determined at 25°C.
There are small, but significant differences between both samples. First, the surface energy is slightly higher for Sheet 1, meaning a stronger non-polar interaction. For both samples, the relative morphology index (RIM) is higher than 1 indicating very clearly the presence of organic coating. The RIM is noteworthy higher for Sheet 1, indicating either more coating or a different distribution or chemical composition of the coated surface. The overall surface polarity (∑ISP), defined by the sum of all interactive specific interactions (ISP), is slightly higher for Sheet 1. This higher polarity is mainly due to the acidic probe chloroform and the basic probes (THF and ether). This can be an indication that the coating layer is not uniform on Sheet 1 compared to Sheet 2 (different distribution of the coating).

At Finite Concentration (FC) isopropanol is injected at 25°C in such a high concentration that the whole surface is saturated. The desorption front is used to calculate desorption isotherms and subsequently the specific surface area using the BET method and range ($0.05 < P/P_0 < 0.2$). The Adsorption Energy Distribution Function (AEDF) is calculated from the desorption profile according to H. Balard [4] (Figure 2).
Table 2 summarizes the surface parameters (adsorbed quantity Q_0, BET surface S_{BET} and constant C_{BET}) determined at 25°C using isopropanol. All the amounts are given for the exposed geometrical surface (28.8 cm^2) determined by the device. The data correspond to the mean value and the standard deviation computed from three IGC-FC measurements.

The higher C_{BET} measured value for Sheet 1 indicates that the interaction ability of isopropanol for the surface is higher. This is in agreement with the IGC-ID results. This is also illustrated by the comparison of the AEDF depicted in Figure 2: Sheet 1 displays slightly more adsorption sites of higher energy (>35 kJ/mol). The measured surface area value is high compared to the geometrical surface area (28.8 cm^2 or 0.00288 m^2), i.e. around 200 times more. This is probably related to the sorption into the coating (sorption into a 3D layer instead on to a surface).

Table 2 - Results of the adsorption of isopropanol on the two metallic sheets

BET method	Sheet 1	Sheet 2
Q_0 [µmol]	2.70 ± 0.05	3.07 ± 0.01
S_{BET} [m^2]	0.525 ± 0.009	0.598 ± 0.002
C_{BET} [n.u]	13.27 ± 0.28	9.56 ± 0.25

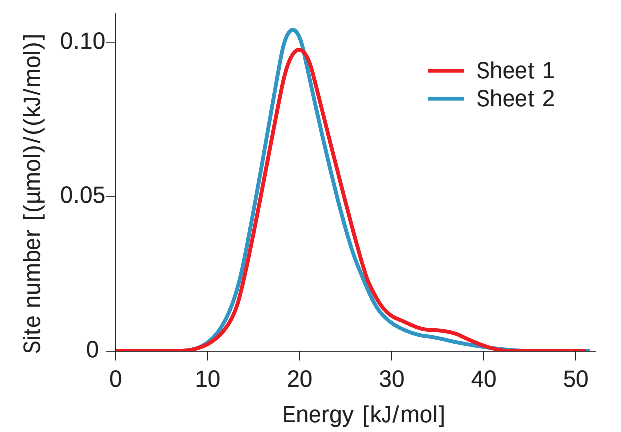

Figure 2 - AEDF obtained with isopropanol at 25°C on Sheet 1 and Sheet 2

Conclusions

This short application note demonstrates clearly that Inverse Gas Chromatography can very well be extended from its classical application domain of powders and fibers to flat materials as coated metallic sheets. This direct measurement of complex surface properties as non-polar and polar interaction behavior, specific surface area and energetic heterogeneity opens the door to many more and very different applications. Herein, organically coated metal sheets were taken as an example. Other applications are polymeric surfaces, modified glassy materials or adhesive surfaces. Whatever the application is, IGC offers a sensitive and quantitative method to determine the surface properties directly of the planar samples – a great advantage for quality control and product development.

References

ref 1. E. Brendlé et al., "Process and equipment for analyzing state of flat or curved surface to determine energy and/or geometric properties of surface using inverse liquid or gas chromatography", *Brevet FR2843803,* **2002**

ref 2. Adscientis, Technical sheet on IGC-ID, **2017**

ref 3. Adscientis, Technical sheet on IGC-FC, **2017**

ref 4. H. Balard, "Estimation of the surface energetic heterogeneity of a solid by IGC method", *Langmuir*, **1997**, 13, 1260-1269

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