# Application of the Chromatographic Step Profile Method for Determination of Water Film Pressure and Surface Free Energy of Quartz

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**Key Words**

Gas chromatography
Step profile method
Adsorption isotherm
Water film pressure
Surface free energy

**Summary**

Investigation of water adsorption by the step profile method (Glueckauf method) was carried out with the help of a modified gas chromatograph equipped with thermal-conductivity detector. On the basis of the adsorption isotherm obtained, the water film pressure and the polar component of the surface free energy of quartz were calculated. The calculated value of the polar component of the surface free energy of quartz agrees with analogous values obtained by other methods.

## Introduction

Surface properties and the type of interactions play a very important role during the process of wetting. Thus, a very important role in this process is also played by the individual components of the surface free energy of solids [1]. The quantity of these interactions determines the properties of a water film on mineral surfaces [2]. The process of wetting the surface of a mineral may be characterized by spreading, immersion and adhesion wetting work [3]. Each wetting process is defined by a certain value of the free energy of the mineral surface corresponding to the amount of adsorbed water. Measurements of water adsorption on mineral surfaces permit the determination of the water film pressure, and thus all components of the surface free energy of solids [2, 4].

In previous papers [1, 2, 4] investigations on the properties of water and calculations of the pressure of a water film and of the surface free energy were presented, including their theoretical interpretation. On the basis of the results obtained by using chromatography with a capacity detector [4] and thermal analysis [2], the pressure of a water film and the polar component of the surface free energy of silica gel [2] and quartz [4] were calculated. The results obtained were in good agreement.

Additional measurements of water adsorption on quartz by a separate and independent chromatographic step profile method (Glueckauf method) with help of a thermal-conductivity detector are presented in this paper. On the basis of the obtained adsorption isotherm, the water film pressure and the polar component of the surface free energy of quartz will be calculated and compared with analogous results obtained by other methods.

## Experimental

For the measurements of water adsorption on quartz surface we have used the chromatographic step profile method (Glueckauf method) [5–8] with a thermal-conductivity detector. A Type N-502 gas chromatograph (made in Poland) was adopted for these investigations (Fig. 1). A water vapour saturator (8) was used to saturate the carrier gas with water vapour at a given temperature.

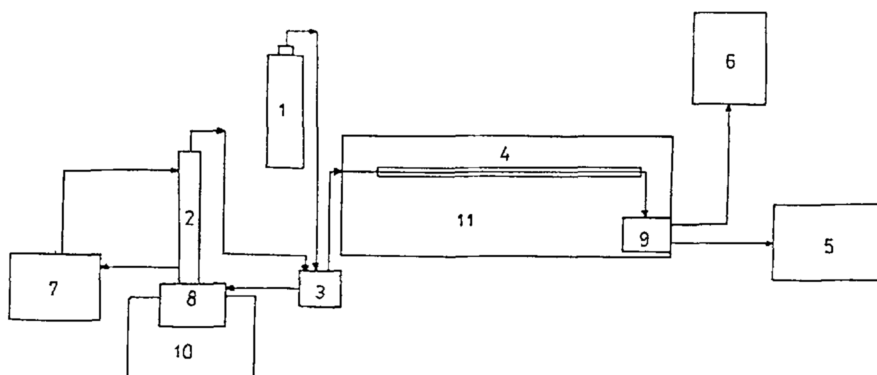


**Fig. 1**
Experimental setup.
**1** hydrogen source, **2** excess vapour rectifier, **3** multi-way valve, **4** chromatographic column, **5** recorder, **6** flowmeter, **7** ultrathermostat, **8** water vapour saturator, **9** thermal-conductivity detector, **10** electric heater, **11** gas chromatograph.



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The measurements were carried out as follows. Hydrogen from a bottle (1) was passed through the saturator filled with heated water (8) where it became saturated with water wapour and its temperature simultaneously increased. In order to bring the mixture to the temperature of the measurement (20°C), it was passed through a cooler (2) connected to a thermostat (7) maintaining its temperature at 20°C. The oven of the chromatograph (11) and the laboratory room were also thermostated at 20°C. Hydrogen saturated with water vapour at this temperature was flowing through a multi-way valve (3) into the chromatographic column (4) packed with the quartz sample. In this way the sample in the column was saturated with water vapour until maximum saturation was reached. The saturation was controlled by the detector (9). With proceeding moistening the recorder (5) was tracing a typical adsorption curve on the basis of the detector signal (see AB in Fig. 2). The moisture in the sample increased during this process reaching a maximum value (saturation state, adsorption maximum, $a_{max}$; the total amount adsorbed up to point B: equilibrium state, the plateau BD in Fig. 2). At this time, the process was reversed and the water was desorbed from the quartz surface. By changing the position of the valve (3), pure hydrogen was introduced into the column, and the recorder was tracing the desorption curve (DF in Fig. 2).

On the basis of the chromatogram the adsorption isotherm was plotted by graphical integration of the corresponding areas in the know way [8]. The amount of water adsorbed on the quartz sample at $p/p_0 = 1$ (saturation state) was calculated from the following equation [8, 9];

$$a_{max} = \frac{c(F \cdot t - V_m)}{m} \quad (1)$$

where c is the concentration of water in the hydrogen stream before the column, $V_m$ is the dead volume of the column, F is the carrier gas flow rate, m is the weight of the quartz sample and t is time.

The $p/p_0$ values were calculated from the corresponding heights of the frontal chromatogram in the known way [8, 9].

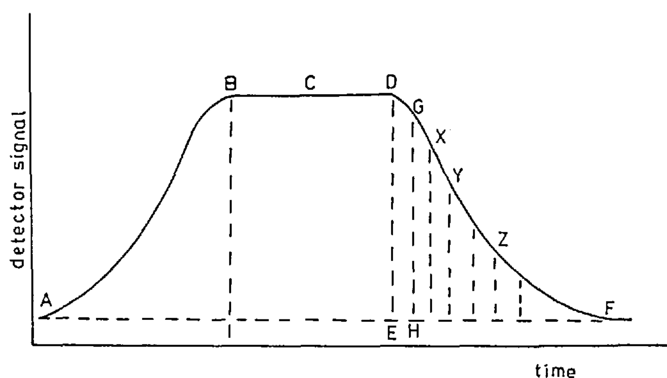


**Fig. 2**
Typical experimental curve.
**AB** adsorption region, **BCD** plateau, **DF** desorption region.

**Materials**

Sample of natural Brazilian quartz powder of high purity for optical purposes (80ppm total impurity level) was used for the investigations. The impurities determined by atomic adsorption spectroscopy were:

$Al_2O_3$: 30ppm
$K_2O$: 10ppm
$Na_2O$: 15ppm
$Li_2O$: 2ppm
$Fe_2O_3$: 5ppm
$TiO_2$: 2ppm
CaO: 8ppm
MgO: 5ppm

The amount of hydroxyl groups (determined by infrared spectroscopy) was about 1 ppm. The 0.15–0.25mm fraction was dried at 150°C for 12 hours and stored in a desiccator. The specific surface area of the quartz determined by the BET method from the thermal desorption of nitrogen was $0.039\,m^2/g$.

## Results and Discussion

Fig. 3 presents the water adsorption isotherm on quartz at 20°C. It is of type II according to the BET classification, which corresponds to the formation of a polymolecular adsorption layer. From Fig. 3 it appears that the maximal adsorption value of water on the quartz surface is $a_{max} \approx 1.5 \times 10^{-2}$ mmol/g. This value corresponds to the adsorption of 16 statistical water monolayers. This was calculated on the basis of the knowledge of the specific surface area of quartz, and assuming that one water molecule occupies an area of 7.06 Å$^2$. This value is in good agreement with the calculation of Fowkes [10] according to which quartz surface can adsorb about 10 statistical water monolayers from the gas phase. These results also agree with analogous results obtained with an apparatus equipped with a capacity detector [11] for the same quartz sample

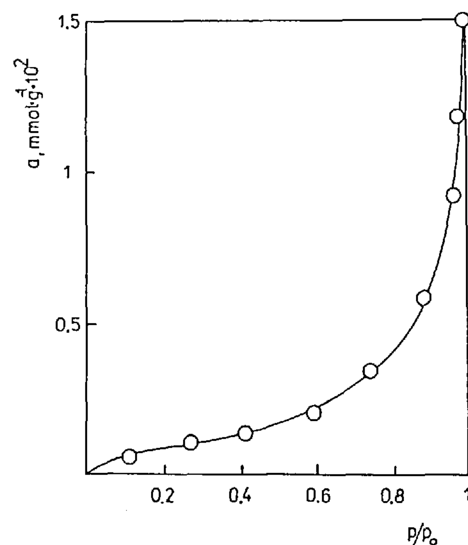


**Fig. 3**
Adsorption isotherm of water vapour on quartz at 20°C.

($a_{max} = 1 \times 10^{-2}$ mmol/g, i.e., 10.7 statistical water monolayers) [4, 12, 13].

The obtained isotherm was used to determine the water film pressure, $\pi$, as a function of water adsorption. In thermodynamics the surface film pressure is defined as [14]:

$$-\pi = \left(\frac{dG}{dA}\right)_{p,T,n} \tag{2}$$

where G is the Gibbs free energy of the adsorbed film, A is the specific surface area of the minerals, p is the equilibrium pressure of the adsorbate and n is the number of moles of a gas or vapour adsorbed on the solid surface at temperature T.

The surface film pressure $\pi$ may be computed from the Gibbs's adsorption isotherm equation:

$$d\pi = RT\frac{a}{A}\, d(\ln p) \tag{3}$$

where a is the amount of the adsorbed gas or vapour in mmol/g and R is the gas constant.

The water film pressure at a given temperature has been evaluated from eq. 3 by integration [4, 14, 15]:

$$\pi = \frac{RT}{A}\int_0^p a \cdot d(\ln p) = \gamma_Q - \gamma_{QW} \tag{4}$$

where a is the water adsorption taking from the adsorption isotherm (where $a = a_1, a_2, a_3, \ldots, a_{max}$), $\gamma_Q$ is the surface free energy of the quartz and $\gamma_{QW}$ is the surface free energy of the quartz covered with the film of water.

In the calculation of the water film pressure, ln p has been plotted against the amount of water adsorbed on the quartz at a constant temperature (20°C) using eq. 4. The area under the curve gives the water film pressure.

Fig. 4 presents the changes in the water film pressure as a function of the adsorption value. From this figure it appears that the $\pi = f(a)$ plot is characterized by inflections occurring at the following film pressure values: 86, 162, 249 and 286 mJ/m$^2$. Analogous inflections in the film pressure – adsorption curves were obtained for the quartz – water system [4] and in a similar system consisting of silica gel and water [2].

The investigations of water film pressure on marble [1], silica gel [2], quartz [4], sulfur [16] and graphite [17] suggest that the steps of the wetting work taking place during water adsorption correspond to the characteristic inflection points on the $\pi = f(a)$ curve. In these papers it has been proven thermodynamically that

$$\pi_S = W_S \tag{5a}$$

$$\pi_I = W_I \tag{5b}$$

$$\pi_A = W_A \tag{5c}$$

$$\pi_{IC} = W_{IC} \tag{5d}$$

and

$$\pi_{max} = W_{max} \tag{5e}$$

where $\pi_s$, $\pi_I$, $\pi_A$, $\pi_{IC}$ and $\pi_{max}$ are the water film pressures following from the spreading, immersional, adhesional, immersional-cohesional and total wetting processes, respectively; the symbol W with the proper subscript represent the corresponding wetting work.

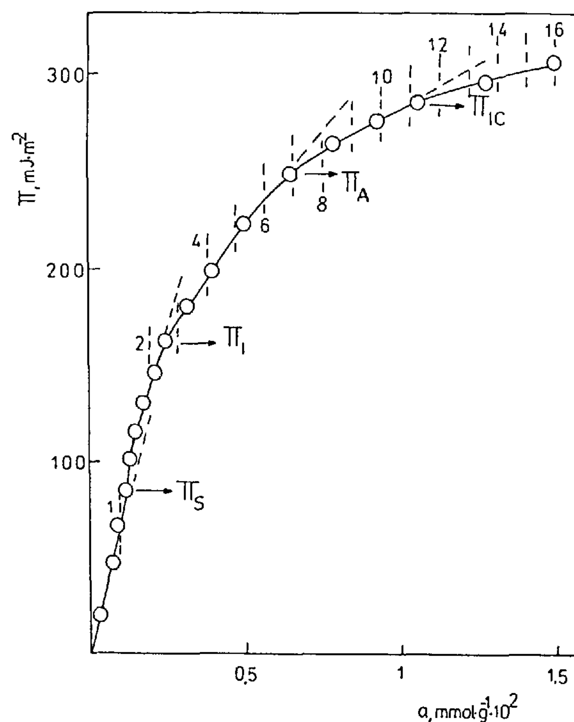


**Fig. 4**

Water film pressure $\pi$ on quartz as a function of the adsorbed water. On the curve, statistical monolayers and characteristic points are indicated: spreading wetting ($\pi_S = W_S$), immersional wetting ($\pi_I = W_I$), adhesional wetting ($\pi_A = W_A$), and adhesional-cohesional wetting ($\pi_{IC} = W_{IC}$).

Accordingly, the inflection points in Fig. 4 can also be assigned to the individual water film pressures specified above. These are listed in Table I together with literature data on silica gel-water [2] and quartz-water [4] systems.

### Characterization of the Individual Steps of the Wetting Process

On the basis of the papers of Fowkes [18–20] and others [1–4, 16, 17] the individual steps of the wetting process can be characterized in the following way.

*Spreading wetting* is a process in which a drop of the water spreads over the quartz. Water when placed on the surface of quartz, both being previously in contact with a fluid phase (water vapour), will tend to spread on the surface if the spreading tension $\sigma_S$ defined by

$$\sigma_S = \gamma_Q - \gamma_W - \gamma_{QW} = W_S \tag{6}$$

is positive. The spreading tension $\sigma_S$ is also equal to the work of spreading per unit area, $W_S$.

In eqn. 6 $\gamma_Q$ is the surface free energy of quartz, $\gamma_W$ is the surface tension of water and $\gamma_{QW}$ is the surface free energy of quartz covered with the film of water. The latter can be defined as

$$\gamma_{QW} = \gamma_Q + \gamma_W - 2\left[\gamma_Q^d \cdot \gamma_W^d\right]^{1/2} - 2\left[\gamma_Q^p \cdot \gamma_W^p\right]^{1/2} \tag{7}$$

where $\gamma_Q^d$ and $\gamma_W^d$ are the respective dispersion components of the surface free energy of quartz and water, and $\gamma_Q^p$ and

$\gamma_W^p$ are the respective polar components of the surface free energy of quartz and water.

Substituting eqn. 7 for $\gamma_{QW}$ in eqn. 6 we can describe the spreading wetting work in a quartz-water system as follows:

$$W_S = 2\left(\gamma_Q^d \cdot \gamma_W^d\right)^{1/2} + 2\left(\gamma_Q^p \cdot \gamma_W^d\right)^{1/2} - 2\gamma_W \quad (8)$$

*Immersional wetting* is a process in which the quartz is covered with the water, both of which were initially in contact with the water vapour, without changing the area of the water-water vapour interfaces. The work of immersional wetting per unit area, or wetting tension, is the work done on the system when the process of immersional wetting involving unit area of the quartz is carring out reversibly:

$$W_I = \gamma_Q - \gamma_{QW} \quad (9)$$

Substituting eqn. (7) for $\gamma_{QW}$ we obtain:

$$W_I = 2\left(\gamma_Q^d \cdot \gamma_W^d\right)^{1/2} + 2\left(\gamma_Q^p \cdot \gamma_W^p\right)^{1/2} - \gamma_W \quad (10)$$

*Adhesional wetting* is the process in which an adhesional joint is formed between two phases. The work of adhesion per unit area is the work done on forming an interface of unit area separated reversibly to form unit areas of each of the water-water vapour and the quartz-water vapour interfaces. The work of adhesion is defined by:

$$W_A = \gamma_W + \gamma_Q - \gamma_{QW} \quad (11)$$

Substituting eqn. (7) for $\gamma_{QW}$ we obtain:

$$W_A = 2\left(\gamma_Q^d \cdot \gamma_W^d\right)^{1/2} + 2\left(\gamma_Q^p \cdot \gamma_W^p\right)^{1/2} \quad (12)$$

*Cohesion wetting* represents the work done when a column of liquid of unit area is split reversibly, normal to the axis of area in contact with the equilibrium the water vapour. Thus, the work of cohesion per unit area, $W_C$, of pure liquid water can be expressed as

$$W_C = 2\gamma_W \quad (13)$$

*Immersional-cohesional wetting* is defined by the following expression:

$$W_{IC} = W_A + \gamma_W = W_I + 2\gamma_W = W_I + W_C \quad (14)$$

Investigations concerning the silica gel water system [2] suggest that the immersional-cohesional wetting process is related to energy changes in the water molecules, which in turn are influenced by the solid surface properties.

The *maximal water film pressure* ($\pi_{max}$) corresponds to the work forming on the quartz surface the water layers possessing the properties of the bulk phase (adsorption equilibrium, maximum of the adsorbed of water):

$$W_{max} = \pi_{max} = W_A + 2\gamma_W = W_A + W_C = W_I + 3\gamma_W \quad (15)$$

or

$$W_{max} = 2\left(\gamma_Q^d \cdot \gamma_W^d\right)^{1/2} + 2\left(\gamma_Q^p \cdot \gamma_W^p\right)^{1/2} + 2\gamma_W \quad (16)$$

**Calculation of the Polar Component of the Surface Free Energy of Quartz**

In order to calculate the polar component of the surface free energy of quartz the following values were substituted into eqns. (8), (10), (12), (14):

$\pi_S = 86\,mJ/m^2$
$\pi_I = 162\,mJ/m^2$
$\pi_A = 249\,mJ/m^2$
$\pi_{IC} = 286\,mJ/m^2$

In addition, we have utilized the following previously determined values [4]:

$\gamma_Q^d = 76\,mJ/m^2$
$\gamma_W^d = 21.8\,mJ/m^2$
$\gamma_Q^p = 51\,mJ/m^2$
$\gamma_W = 72.6\,mJ/m^2$

The calculated values of $\gamma_Q^p$ are: 103.6, 115.1, 137.4 and 84 $mJ/m^2$, respectively, with an average value of 110.3 $mJ/m^2$. This value is in good agreement with analogous values obtained from separate and independent experiments (Table I) in quartz-water system [4] (115 $mJ/m^2$) and in a similar system of silica gel-water [2] (114.67 $mJ/m^2$).

**Table I** Comparison of the results calculated for the water film pressure ($mJ/m^2$) and the average component of surface free energy ($mJ/m^2$), for quartz and silica gel.

| | Silica gel | Quartz | |
|---|---|---|---|
| | Thermal analysis [2] | Step profile method with capacity detector [4] | Step profile method with thermal-conductivity detector (present work) |
| $\pi_S$ | 82.7 | 96 | 86 |
| $\pi_I$ | 182.7 | 162 | 162 |
| $\pi_A$ | 230.7 | 227 | 249 |
| $\pi_{IC}$ | 296 | 294 | 286 |
| $\pi_{max}$ | 386.1 | 380 | 307.2 |
| $\gamma_Q^p$ (average) | 114.67 | 115 | 110.3 |

## Conclusion

A modified gas chromatograph permitted the simple and precise measurement of the value of water adsorption. An important advantage of this apparatus is the possibility of its application for the general measurements of liquid adsorption on solids with widely different particle sizes and specific surface areas. With the help of this apparatus the adsorption phenomena at constant temperatures and the properties of surface liquid layers (e. g. liquid film pressure, surface free energy, adsorption capacity, adsorption kinetics, etc.) can be investigated. The knowledge of these properties is not only of great importance in chromatography, but also in physical chemistry and chemical technology (adsorption, catalysis, enrichment of useful minerals).

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