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## CHROMATOGRAPHIC METHOD FOR STUDYING THE HYGROSCOPIC QUALITIES OF SOLIDS\*

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### SUMMARY

The features and advantages of chromatographic methods for investigating the complex water vapour sorption and desorption processes of soluble salts and mineral fertilizers were examined. Adsorption and absorption stages of the process were found, the sorption isotherms and chemisorption contributions were defined, the formation of a saturated solution film on the salt surface was demonstrated and the water desorption kinetics were studied. A chromatographic method for determining fertilizer moisture and hygroscopicity as quality characteristics was developed.

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### INTRODUCTION

Gas chromatography can be used for the investigation of the thermodynamics and kinetics of processes in gas–condensed phase systems and for the determination of practical indicators of product quality<sup>1–7</sup>.

Hygroscopicity, defined by the characteristics of water vapour sorption and desorption processes, is one of the most important properties of soluble salts and salt-based fertilizers. The conventional methods (gravimetric and chemical determinations) are time consuming and labour intensive and characterize only the overall process<sup>8,9</sup>.

It is more appropriate to apply chromatographic methods, being highly informative, sensitive and rapid, to physico-chemical investigations of the soluble salt–water vapour system and for the rapid evaluation of the moisture content and hygroscopicity of salts and fertilizers as indicators of their quality. The application of chromatography to the above-mentioned systems requires the development of special modifications.

### EXPERIMENTAL

One of the methods for studying the sorption process is the impulse method, in

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which a water vapour zone of initially rectangular shape is introduced into a column packed with the salt being examined and the peculiarities of its broadening as a result of sorption interactions are observed. The thermal desorption process was studied by observing the transfer of water from the specimen directly into a thermal conductivity detector and registering it as an elution curve.

The hygroscopic qualities of potassium chloride and nitrate, ammonium nitrate and dihydrogenphosphate, potassium dihydrogenphosphate and nitrogen-phosphorus-potassium (NPK) fertilizers were investigated, and it was found that the specific salt surface areas, measured by low-temperature nitrogen adsorption from a mixture with helium, are in the range 0.1–0.2 m<sup>2</sup>/g. The apparatus used was essentially as described earlier<sup>5,6</sup>.

For studying water vapour sorption, a specimen of salt of given dispersity was packed into the thermostated column of 3 mm I.D., directly ahead of the detector cell; the salt was heated before the experiment in a flow of carrier gas (at 60–80°C, depending on the thermal stability of the salt), until water ceased to be evolved. To create a water vapour zone of given constant concentration, sufficient water was introduced on to an inert layer of particles in the range 0.1–0.5 mm (melted quartz). The quartz layer, in which a primary rectangular impulse is formed, was placed on the net partition of the column directly above the specimen under examination. The stepwise elution curve obtained is presented in Fig. 1, curve 1. As can be seen, the broadening of the rear edge of the zone on the quartz and on the salt (CD) under investigation (curve 2) coincide. The broadening of the front edge AB (curves 2 and 3) differs from that for curve 1. The deviation of the front edge on curve 1 from the rectangular shape at a dead volume of the system  $\leq 5$  ml and a carrier gas velocity  $\leq 50$  ml/min does not exceed 7% [being evaluated as the area ratio AFB:ABCD (curve 1)]. The height of the step is directly proportional to the saturated water vapour pressure at the given temperature; the reproducibility of this calibration method is  $\pm 5\%$ .

Fig. 1 shows a typical chromatogram for water on the soluble salt (curve 2). By varying the conditions of solid and gaseous phase contact in a number of special experiments, it was found that it is possible to obtain a chromatogram for the salts

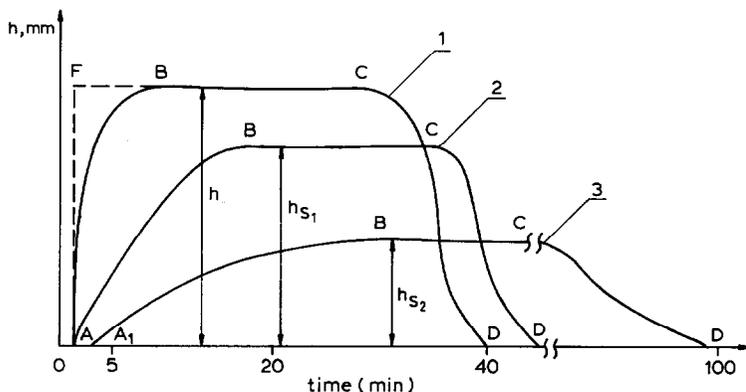


Fig. 1. Water chromatograms at 20°C: 1, Quartz particles; 2, potassium chloride; 3, NPK fertilizer. Step heights:  $h$ , for quartz;  $h_{s_1}$ , for potassium chloride;  $h_{s_2}$ , for NPK fertilizer.

studied, the shape of which, being mostly a result of equilibrium factors, characterizes the process of reversible sorption and does not depend on the experimental conditions (carrier gas velocity 30–80 ml/min, weight of salt 1–10 g, salt dispersity 0.05–0.1 mm, water introduced 1–20 mg).

In a series of experiments carried out to study the desorption kinetics, conditions were chosen such that the height of the detector signal was proportional to the rate of evolution of the volatile component (water)<sup>6</sup>. It was shown that with a weight of salt or fertilizer not exceeding 10 mg and a carrier gas velocity less than 60 ml/min, the time delay was 15 s and the effects of external diffusion and the distortion of the shape of the kinetic curve due to broadening in the dead volume were negligibly small.

## RESULTS AND DISCUSSION

One can single out three parts of the equilibrium chromatogram (Fig. 1, curve 2). AB, corresponding to the broadening of the front edge of zone AB, characterizes the initial stage of the sorption process, then the horizontal section BC is registered, corresponding to a constant vapour pressure above the salt; the broadening of the rear edge of zone CD coincides with that obtained in the control experiment. The independence of the results obtained of the contact conditions of water vapour with the salt under investigation permits the conclusion that the contribution of kinetic factors to the broadening of the zone is insignificant.

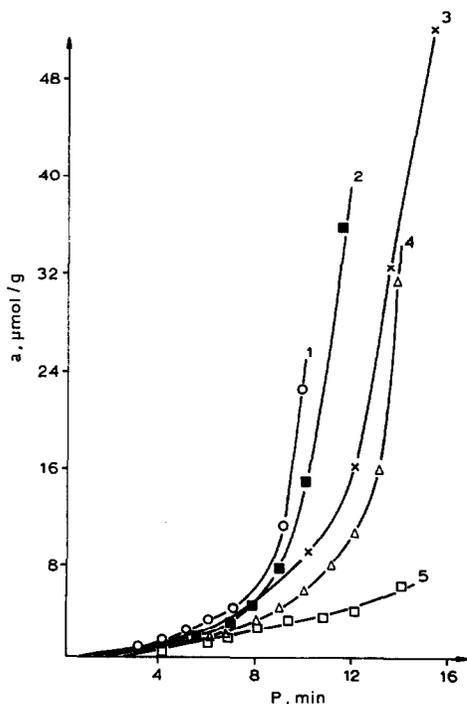


Fig. 2. Water vapour sorption isotherms for salts at 20°C: 1,  $\text{NH}_4\text{NO}_3$ ; 2,  $\text{KNO}_3$ ; 3,  $\text{KH}_2\text{PO}_4$ ; 4,  $\text{KCl}$ ; 5,  $\text{NH}_4\text{H}_2\text{PO}_4$ .

Having assumed that this is an adsorption process, the isotherm calculation method for the broadened boundary of the elution curve was applied to define the nature of the initial stage of the sorption process<sup>4</sup>; the isotherm, with its convex part facing the vapour pressure axis, corresponds to the broadening of the front edge of the chromatogram. In Fig. 2, the isotherms of water vapour adsorption on the salts studied at 20°C are shown.

From the equilibrium pressure dependence on temperature in the range 10–30°C for section AB the isotherms and differential heats of adsorption were calculated; they were in the range 17–42 kJ/mol for the salts studied.

The results for the initial process stage can be interpreted as follows. On contact of water vapour with the preliminarily dehydrated salt a certain amount of water is chemisorbed on the especially active areas of the surface. This is accompanied by modifications of the surface, which increases its homogeneity. This can be seen from the shape of the isotherms obtained, which is typical of adsorption on a non-specific homogeneous surface with a relatively high interaction between the adsorbate's molecules<sup>10</sup>.

The first stage is completed with the formation of a sorption film (80–100 molecular layers), where a constant concentration of water vapour is established above the salt surface (section BC of the chromatogram, Fig. 1). Special experiments showed that this constant concentration corresponds to the equilibrium vapour pressure above the saturated solution film on the salt surface. Comparison of the data obtained with those in the literature confirmed the formation of a surface saturation solution film and equilibrium between the condensed and gaseous phases on section BC of the chromatogram. The heat of evaporation of water for a potassium chloride saturated solution, calculated from the dependence of the heights ( $h$ ) of the horizontal parts of stepwise elution curves on temperature (Fig. 3), agrees satisfactorily with that calculated from results<sup>11</sup> obtained by the static method ( $44 \pm 2$  and  $42 \pm 2$  kJ/mol, respectively). Therefore, the nature of the second stage is defined by the properties of the surface saturated salt solution.

When a salt is stored under conditions such that  $P_{\text{H}_2\text{O}} \gg P_s$  (where  $P_{\text{H}_2\text{O}}$  and  $P_s$  are the pressures of water vapour in the gaseous phase and above the saturated salt

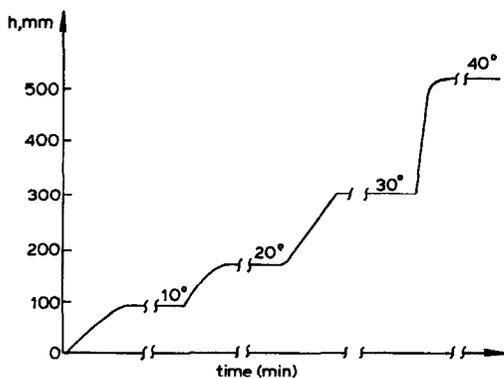


Fig. 3. Dependence of water step height on temperature in potassium chloride.

solution, respectively), the sorption process proceeds accompanied by a decreasing concentration in solution at the gas-liquid boundary.

Curve 3 in Fig. 1 depicts a typical water vapour sorption chromatogram for NPK fertilizers. In contrast to pure salts, a significant broadening of the front and rear edges of the chromatographic zone is observed. Special experiments showed that sections AB and CD present the sorption process under non-equilibrium conditions; however, the step height  $h_{s_2}$  (section BC) is directly proportional to the vapour pressure above the saturated solution on the surface of the fertilizer particles.

The stepwise chromatograms obtained, characterizing the features of the surface saturated solutions permitted a chromatographic method to be developed for the definition of the hygroscopic points ( $G$ ) of salts and fertilizers, which are the basis for their hygroscopicity evaluation<sup>8</sup>:

$$G = \frac{P_s}{P_{H_2O}} = \frac{h_s}{h_{H_2O}} \cdot 100$$

where  $P_s$ ,  $h_s$  and  $P_{H_2O}$ ,  $h_{H_2O}$  are the water vapour pressures above the saturated surface solution and the step heights for the sample examined and calibration graph 1, respectively. The  $G$  values of salts and fertilizers allow absorption capacities under storage conditions to be correlated and predicted. Studies of the kinetics of water desorption from the salt or fertilizer showed that both the rate and amount of water desorbed (Fig. 4) are a function of temperature, which indicates non-homogeneity of the salt surface. Complete evolution of hygroscopic water is achieved at 65–80°C. The amount of water chemisorbed from the water impulse constitutes 20–40% of the total sorption. The apparent activation energy of the desorption of chemisorbed water is determined as 70 kJ/mol. The investigation of water desorption kinetics led to the conditions for the determination of salt and fertilizer moisture content from the area under the elution kinetic curve obtained by the chromatographic method.

Determinations of moisture content and hygroscopic point by the chromato-

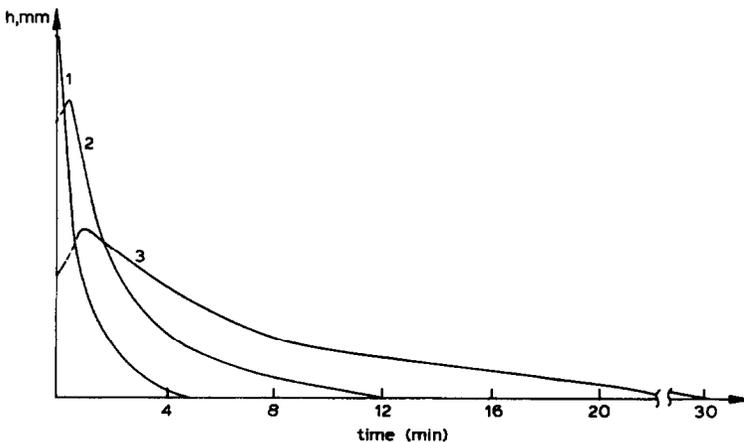


Fig. 4. Kinetic curves of thermal desorption of water from NPK fertilizer at (1) 30°C, (2) 50°C and (3) 70°C.

graphic method can be carried out on a single specimen in one experiment. The determination time is 30–40 min, including a time for moisture determination of 15 min, with a root mean square variation of  $\pm 3\%$ .

Chromatographic methods for determining the hygroscopic features of salts and fertilizers have found application in both laboratory and industry practice. Such chromatographic methods have allowed the specific features of water vapour sorption and desorption processes in complicated gas–liquid–solid systems formed by the interaction of water vapour with soluble salts and fertilizers to be examined, and also a rapid instrumental method for hygroscopic determination of substances of this type to be developed.

The results of this work indicate more extensive practical applications of gas chromatography.

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