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Special Reviews

DETERMINATION OF WATER CONTENT BY MEANS OF THE DERIVATOGRAPH

J. SIMON

Institute for General and Analytical Chemistry of the Technical University, Budapest, Hungary

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The determination of water content by means of the Derivatograph is treated in the paper. The determination of water in analytical precipitates, various pharmaceutical products, biological substances, the products of food industry is treated on the basis of some practical examples. The applicability of the Derivatograph for determining the adsorption capacity of industrial adsorbents, the hydration conditions of cement, the system $Ca_3A-CaSO_4 \cdot H_2O$ and the rehydrability of clay minerals is demonstrated. The aluminium oxide barrier layers were investigated on the basis of the water content of the aluminium hydroxide. For the characterization of the different strengths by which water is bound in strontium chloride hydrates the apparent activation energies are also presented.

Thermal methods of drying have long been used to determine the moisture in solid substances. In the case of both the direct and indirect determinations the moisture is generally removed from the substance by heating; in the first case the water is bound by an adsorbent and the weight increase is measured while in the second the residue is weighed. These water determinations can be made under isothermal or non-isothermal, dynamic conditions, or in their combination.

In the past nearly fifteen years the Derivatograph [1] has been successfully used in the determination of moisture. Taking into account that in the course of thermal analysis only thermal energy is transmitted to the sample, the temperature at which the water is released is to a first approximation characteristic of the strength of bonding of the water. On this basis the relatively loosely bound water (adhesion, inclusion, adsorption) which is released at a relatively low temperature can be distinguished from strongly bound water (zeolitic, crystal and structural) which is lost at a higher temperature.

The present paper is a survey of the fields in which this complex thermal apparatus has been applied to the determination of water bound by the different forces.

The device has been widely used to investigate the structures and thermal behaviours of precipitates used in gravimetric analysis [2—4]. Some bivalent metal ions, such as Mg^{2+}, Mn^{2+}, Be^{2+}, Cd^{2+}, Zn^{2+} and Co^{2+} give precipitates with diammonium hydrogen phosphate in an aqueous solution containing ammonium chloride. The thermal decompositions of the ammonium phosphate precipitates of the various ions proceed very similarly. In Fig. 1 are shown the decomposition

curves of magnesium ammonium phosphate. The precipitate contains two moles of water of crystallization. This water is released in two steps, the removal of the second mole of water trailing on up to 300°. The removal of the structural water formed in the course of the reaction is indicated by a DTG maximum at 510°.

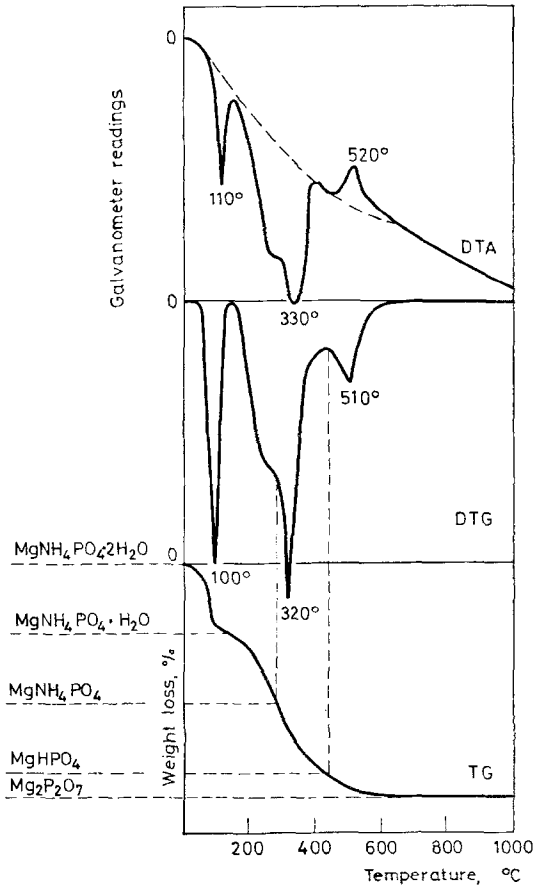

Fig. 1. Thermoanalytical curves of $MgNH_4PO_4 \cdot 2H_2O$

The Derivatograph has been used to determine the moisture and structural water in a number of analytical grade reagents and the temperatures at which these materials can be dried without decomposition [5–7]. The thermal decomposition curve of sodium thiosulphate is presented in Fig. 2. A peak at 30° on the DTA curve indicates the incongruent melting point of the investigated sample. The water of crystallization leaves in two stages up to 240°.

The moisture contents of powdered drugs and granulated pharmaceutical products must be known and controlled before tabletting. The tablets crumble if the

water content is lower than an optimum value, but if it is too high the powder or granulate cannot be tabletted [8]. Lactose is often used as vehicle; besides mechanically bound water this also contains 1 mole of water of crystallization. The amount of mechanically bound water is dependent on the relative humidity of

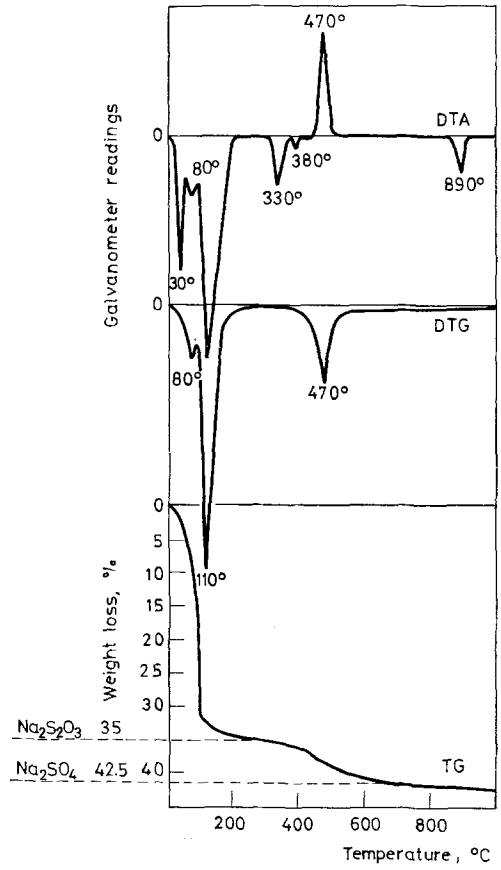

Fig. 2. Thermoanalytical curves of $Na_2S_2O_3$

the air, whereas the amount of crystal water is independent of it, as indicated by the TG and DTG curves of Fig. 3

In determinations of the active ingredients in pharmaceutical products the moisture contents have to be known as well. Examples of this field are the estimations of vitamin B_{12} [9] and cadmium thiobarbiturate [10]. The thermoanalytical decomposition curves of vitamin B_{12} recrystallized from acetone are presented in Fig. 4. An inflection point can be observed at 60° in the DTG curve; on the basis of this the acetone content of the sample can be more or less established as 4%. From the TG curve it can be said that the sum of water and acetone is 20%.

In the technology of a number of pharmaceutical products the final process is recrystallization from an organic solvent. These products may therefore contain adsorbed water and solvent of crystallization as well. The removal of water and solvent proceeds simultaneously or in overlapping processes in nearly the same

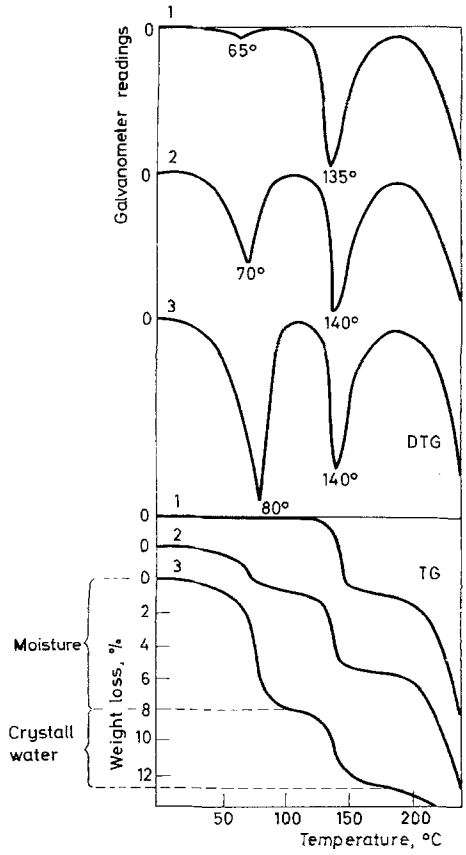

Fig. 3. Thermoanalytical curves of lactose containing various amounts of adsorbed water

temperature interval during thermal treatment, and cannot be separated by means of the TG and DTG curves. The TG curves show the total weight loss due to the removal of the two substances.

By the use of the thermo-gas titrimetric attachment [11] the water can be determined quantitatively, and if the thermo-gas analyzer is attached to the Derivatograph direct water determination can be made continuously [12]. The essence of this technique is as follows: From a furnace narrowed by a silica bell in order to prevent gas permeation the gases evolved during thermal decomposition are continuously pumped through a tube and a sintered gas frit to the absorber, and

the device is flushed by inert gas dried over concentrated sulphuric acid. Gaseous products absorbed in a mixture of propanol and pyridine are titrated with Karl-Fischer reagent using dead-stop end-point detection. Water can be determined by this method in the presence of CO, CO_2, SO_2, SO_3, CH_3COOH and HCN.

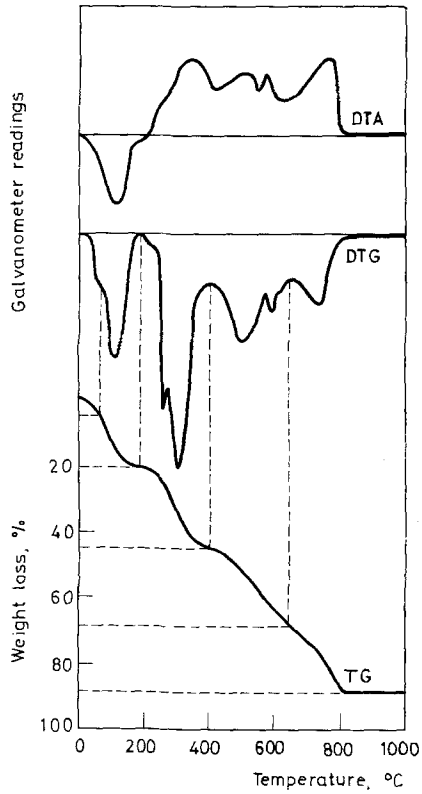

Fig. 4. Thermoanalytical curves of vitamin B_{12}

The Derivatograph has successfully been used to study the moisture contents of biological substances [13, 14]. From the amount of water released during the thermoanalytical decomposition of oxalate-type kidney stones, the compositions of the kidney stones can be determined [15].

The adsorption capacities of various industrial adsorbents can be investigated by measuring the weight loss accompanying the desorption due to heating [16]. Molecular sieve samples with different water contents have been investigated and it has been found that samples containing less than 5% water exhibit a thermal behaviour different from that of samples with higher moisture content. The thermal curves of the Hungarian-made molecular sieve Klinosorb-4 are presented in Fig. 5. The weight of the sample with low water content is practically constant

up to 100°. In the case of higher water contents the maximum rate of weight loss is at 80°, as shown by the DTG curve, whereas with samples of lower moisture content the peak indicating the above-mentioned process is shifted to about 200°. This suggests that up to 5% water content the Klinosorb-4 molecular sieve binds

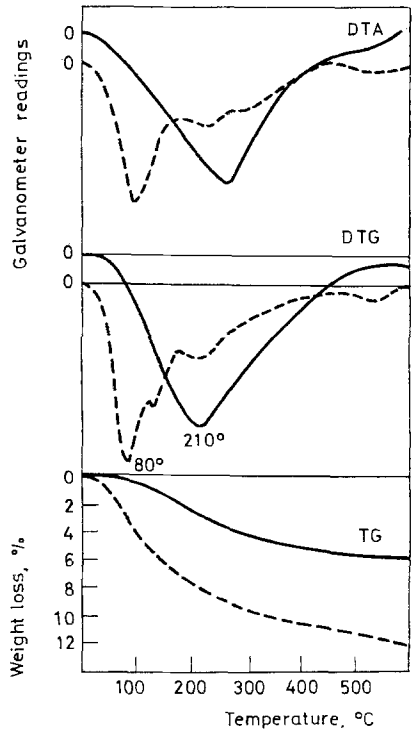

Fig. 5. Thermoanalytical curves of Klinosorb-4 molecular sieve; ——— low moisture content, - - - - - high moisture content

water as zeolitic water, whereas the moisture above this level is bound by adsorption.

Investigations by means of the Derivatograph provide an opportunity of detecting the presence of crystalline and amorphous aluminium hydroxides in aluminium oxide barrier layers formed by anodic oxidation of aluminium, i.e. of clarifying the composition of the γ_1-Al_2O_3 phase [17]. Fig. 6 presents the TG and DTG curves of such an aluminium oxide barrier layer. Amorphous $Al(OH)_3$ loses its water content at a low temperature, the maximum rate of weight change being at 60°. Hydrargillite releases its three moles of water of crystallization at maximum rate at 330°, and boehmite its one water mole at 530°. The stages of water release can be well distinguished by means of the DTG curve. On the basis of the weight

losses corresponding to the steps, the amounts of amorphous and crystalline aluminium hydroxide and oxide hydrate can be calculated.

Determination of moisture in food industry products is also an important field of application of the apparatus. Experiments have been carried out to determine

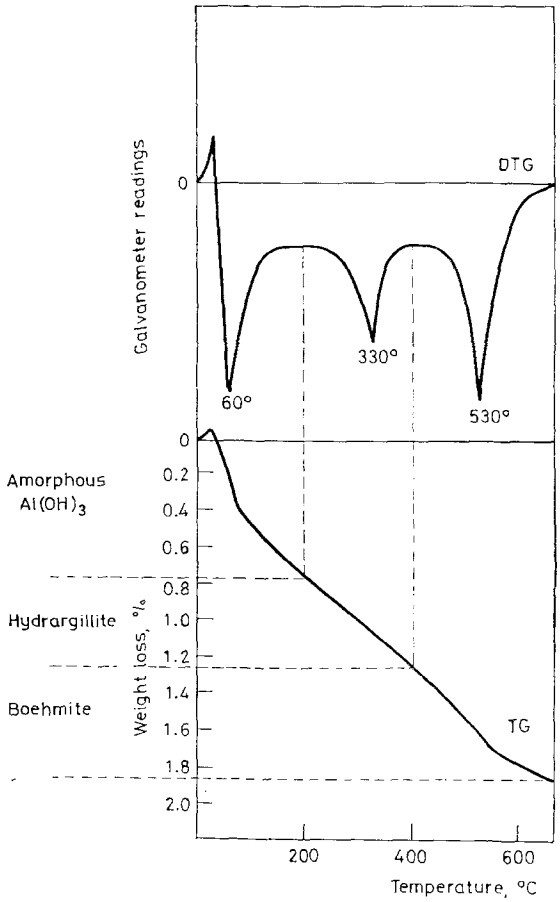

Fig. 6. Thermoanalytical curves of aluminium oxide barrier layer

water in butter, cream, cheese, milk powder and meat products using the Derivatograph [18].

Investigations are in progress on the behaviour of food products – with special regard to dried fruits and vegetables – in closed spaces with different humidities [19].

The Derivatograph can be well used to study the hydration conditions in cements [20].

The hydration of the $Ca_3A-CaSO_4 \cdot H_2O$ system has been studied with regard

to different gypsum contents and different temperatures, the effect of freezing and steaming and the effect of hydration time [21–23].

The rehydrability of clay minerals (illite, hydromuscovite, bentonites, and montmorillonite) has been investigated [24]. The influence of mechanical load

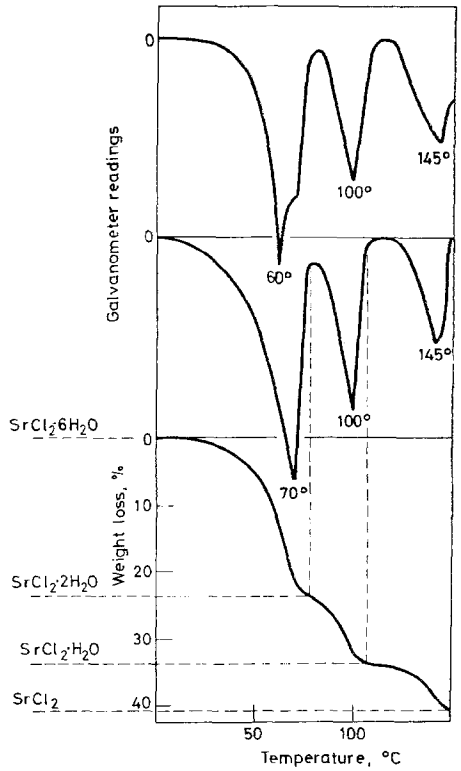

Fig. 7. Thermoanalytical curves of $SrCl_2 \cdot 6H_2O$

on $MgSO_4 \cdot 7H_2O$ has also been studied [25]. It has been established that in the case of various salt hydrates changes of different degrees take place as a function of time. Accordingly, for analytical studies only small crystals may be used which are not loaded mechanically.

The mechanism of the release of crystal water from alkaline earth halide hydrates has been studied and the apparent activation energies of the stages of water removal have been calculated [26]. As an example, the decomposition curves of strontium chloride hexahydrate are presented in Fig. 7. It can be seen that the water crystallization leaves in three steps. The total weight loss corresponds to the stoichiometric amount of water if the sample has not been pulverized previously. At a heating rate smaller than 3°/min when the water vapour can leave

the air space without difficulty, 4, 1 and 1 moles of water leave in the first, second and third steps, respectively.

The apparent activation energies of the release of the first four, the fifth and the sixth moles of water are 24.9, 37.5 and 43.0 kcal/mole, respectively.

The first four moles of water are removed from the melt phase and the final two from the solid phase.

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RÉSUMÉ — L'article traite de la détermination de la teneur en eau à l'aide du "Derivatograph". La méthode est exposée en se servant d'exemples pratiques comme les précipités analytiques, divers produits pharmaceutiques, alimentaires, des substances biologiques. On montre que le "Derivatograph" peut être utilisé pour déterminer la capacité d'adsorption des adsorbants industriels, pour examiner l'hydration du ciment, du système $Ca_3A-CaSO_4 \cdot H_2O$ et la rehydration des minéraux argileux. Examination des couches interfaces d'oxyde d'aluminium sur la base de la teneur en eau du hydroxide d'aluminium. L'énergie d'activation apparente a été déterminée et utilisée pour caractériser les différentes forces de liaison de l'eau dans les chlorures alcalino-terreux hydratés.

ZUSAMMENFASSUNG — Die Bestimmung von Wasser mit Hilfe des Derivatographen wurde besprochen. Es wurden die verschiedenen Anwendungsmöglichkeiten der Methode, wie die Bestimmung des Wassers in analytischen Niederschlägen, Arzeneimitteln, Lebensmittel, biologischen Substanzen an Beispielen besprochen. Die Anwendbarkeit des Derivatographen zur Bestimmung der Adsorptionskapazität von industriellen Adsorbenten, der Hydrationsverhältnisse von Zement, des Systems Ca_3A—$CaSO_4 \cdot H_2O$ und der Rehydration von Tonminera'ien wurde erörtert. Aluminiumoxydgrenzschichten konnten auf Grund des Wassergehalts des Aluminiumhydroxyds geprüft werden. Zur Charakterisierung der verschiedenen wasserbindenden Kräfte werden die Werte der scheinbaren Aktivierungsenergien der Alkalierdchlorid-hydrate vorgelegt.

Резюме — Описан способ определения воды с помощью дериватографа. Изучение проведено для выяснения применимости прибора в этих целях. На ряде практических примеров показано определение воды, находящейся в аналитических осадках, различных лекарствах, биологических материалах. Отмечена применимость дериватографа для определения адсорбционной емкости промышленных адсорбентов. Приведены величины кажущейся энергии активации для характеристики различных сил, связывающих воду в гидратах щелочноземельных хлоридов.