ANALYSIS OF GASEOUS MIXTURES BY THERMAL DESORPTION FROM THIN LAYERS OF MOLECULAR SIEVES

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The method of thermal desorption from thin layers of molecular sieves has been applied for quantitative analysis of gaseous mixtures at low pressures. Experimental arrangement as well as analytical procedure are described. The applicability of the method is demonstrated by the results obtained for several different gaseous mixtures.

In studies of heterogeneous catalytic reactions and reactions in gaseous discharges the pressure of the gaseous phase is frequently considerably lower than the atmospheric pressure. If then the classical gas-phase chromatography is used to analyse the gaseous phase, the sample has to be compressed before the injection into the column to a pressure approximately equal to that of the carrier gas[1] and the amount of the gas sample is usually so small that very sensitive detectors must be used. Another possibility which makes use of differences in the adsorption isobars[2] of various components of the gaseous mixture on molecular sieves represents the method of thermal desorption. An advantage of this method is a possibility of a quick analysis of a gas mixture directly at low pressures using a simple experimental arrangement.

Using a column or an ampule filled with granules of a molecular sieve proved itself unsuitable in view of a rather bad heat transfer between the granules. Therefore, experiments described in this paper were carried out using a thin layer of the molecular sieve deposited directly onto the inner wall of the adsorption ampule[3]. The cited laboratory note[3], however, lacks any information on experimental arrangement (the way of gas doses introduction, method of desorption, detector used *etc.*) which are — as we observed — of principle importance in carrying out the analysis successfully.

EXPERIMENTAL AND RESULTS

The experimental arrangenent used in this study is shown in Fig. 1. The section of the apparatus separated from the sorption ampule S with a layer of the molecular sieve (*i.e.* the reservoirs R_1, R_2; the valves V_3 through V_8; the thermocouple gauge (TM) served to prepare gaseous mixtures of a desired composition in the volume closed by the valves V_3, V_4, and G_2. Also, in this section the coil of the high-frequency transformer was located which was used to study effects of discharge on the gaseous mixture composition. The volume of the internal part of the dosing valve G_2 (a glass vacuum stopcock) determined the analyzed dose of the gaseous mixture. The optimum amount (Q) depends for a given mixture on its composition, the amount of the sieve, the concentration range over which the particular indicator can be used, and the sensitivity of the indicator towards various components of the mixture. In the described experimental arrangement and for

the mixtures studied $Q = 3 . 10^{-3} - 5 . 10^{-2}$ Torr l. For an unknown mixture, Q may be easily estimated from the results of a few test measurements. Decreasing the dose size lead to a shift of the desorption curve maximum towards higher temperatures. The sieve 13 X proved itself to be the most suitable from various types tested. Granules of this sieve were powderized and a suspension in ethanol was prepared from this powder. About 1 ml of this suspension was introduced into the glass ampule (volume about 3 cm³), and a thin layer of the sieve of $3-5$ cm² geometrical area was obtained by evaporating of ethanol while rotating the ampule. The weight of the molecular sieve layer was $10-80$ mg, most suitably about 30 mg. However, the molecular sieve does not have to be weighted beforehand, as the optimum layer thickness can be — with some experience — estimated visually, and small deviations do not lead to changes in the desorption spectrum (by increasing the sieve weight, the desorption maxima shift towards higher temperatures). As an indicator a Penning gauge was used (type KJ, ILM Labor, DDR, operating pressure range $10^{-5}-10^{-3}$ Torr) connected to a recorder (type BT-1, MAW, DDR, operating voltage range $0-5$ mV).

The outlet of the sorption ampule was connected by a glass tube through the valve G_1 directly to the region between the electrodes of the Penning gauge PM. It is important to keep the volume between the valves G_1, G_2, the internal volume of G_2, and the volume of the line between G_1 and the gauge as small as possible; otherwise, the width of desorption peaks increases, the overlap of peaks occurs, and consequently the resolution power decreases. In the set-up described here the sum of the above mentioned volumes was about 4·5 cm². The apparatus was pumped by the oil diffusion pump D, backed by the rotary oil pump A or the cryoscopic unit C (an ampule filled up with active charcoal and cooled by liquid nitrogen).

When carrying out the analysis, the ampule was first pumped down to about 10^{-5} Torr and heated up to about 100°C to degas the sieve. (When a freshly prepared sieve is used for the first time, or when higher and unsaturated hydrocarbons are analyzed, degassing should be done at higher temperatures — about 400°C.) The valve G_1 was then closed and the sieve was cooled by liquid nitrogen. Thereafter, a dose of the analyzed mixture was admitted. After about one minute the valve G_1 was opened. The presence of hydrogen was indicated by a sudden increase of the ion current of the Penning gauge (hydrogen, and similarly helium or neon, are practically not sorbed by the sieve at the liquid nitrogen temperature). The liquid nitrogen bath
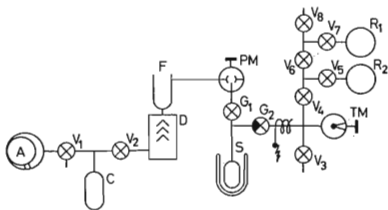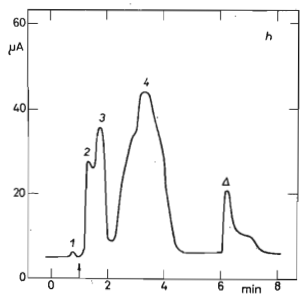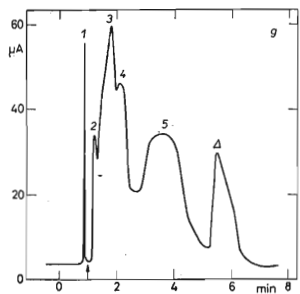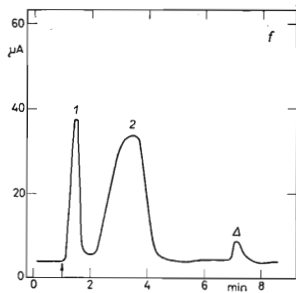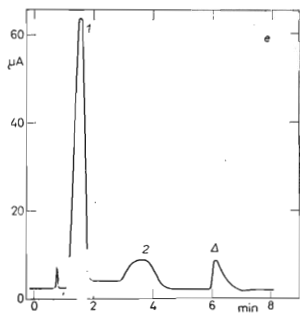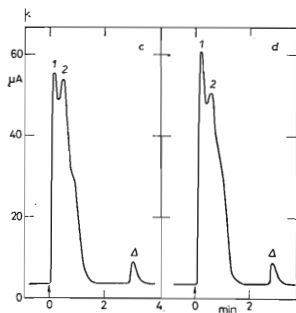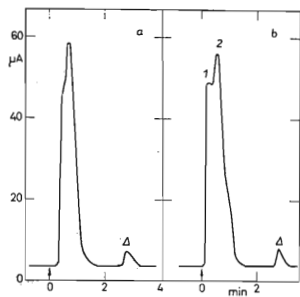

FIG. 1

Apparatus Used in Studies of Thermal Desorption from Thin Molecular Sieve Layers

Description see the text. The figure shows also the location of the secondary coil of the high-frequency transformer used in studies of gas discharge reactions.

was then removed and the ampule with the sieve was let to warm up to room temperature. A gradual desorption of components of the mixture occurred. The dependences of the gauge ion current on time are in Fig. 2 for several different mixtures. The corresponding changes in the ampule wall temperature are given in Fig. 3. Let us note here that the temperature of the desorption curve maximum of a particular component varies slightly with the over-all composition of the mixture. Hydrocarbons of higher molecular weights, namely unsaturated hydrocarbons, desorb at higher temperatures than the laboratory temperature. Therefore, it is necessary in such cases to continuously increase the temperature of the sorption ampule up to about 100°C using a small oven with a temperature-programmed control unit.

Fig. 3

Dependence of Temperature of the Ampule with Molecular Sieve on Time during Gas Desorption
    Measured by means of the iron–constantan thermocouple attached to the ampule surface.
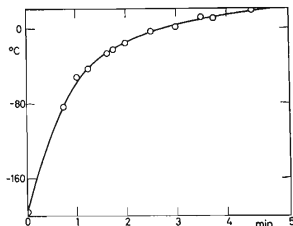
From the height of the desorption maximum the amount of the particular component in the mixture can be estimated. However, this can be done only after calibration by the mixture of a known composition. The dependence of the desorption maximum height (or the area beneath the desorption curve) on the amount of the component in the mixture is not linear and thus the application of the thermal desorption method (in the arrangement described here) does not seem to be suitable for the purposes of quantitative analysis. In conclusion, let us note that a theoretical analysis of desorption spectrometry of gases from molecular sieves has appeared recently[4].

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    Translated by Z. Herman.

Fig. 2

Dependence of the Ion Current on Time during Thermal Desorption from a Thin Molecular Sieve Layer

    Δ Increase of the sieve layer temperature to about 90°C; the arrow indicates when the liquid nitrogen bath was removed; *a* pure nitrogen; *b* mixture: 15% oxygen (1), 85% nitrogen(2); *c* 30% oxygen(1), 70% nitrogen(2); *d* 60% oxygen(1), 40% nitrogen(2); *e* 85% methane(1), 15% ethylene(2) (ethylene used contained several percents of hydrogen); *f* 20% methane, 80% ethylene(2); *g* 50% hydrogen(1), 5% nitrogen(2), 30% methane(3), 10% carbon monoxide(4), 5% carbon dioxide; *h* 3% hydrogen(1), 10% oxygen(2), 40% nitrogen(3), 47% ethylene(4).