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# UHV FACILITY FOR THERMAL DESORPTION SPECTROSCOPY AT LOW TEMPERATURES

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A design of a simple ultrahigh vacuum apparatus with a facility for thermal desorption spectroscopy (TDS) is described. The most important technical details concerning the pumping system, working chamber and related electronics are presented. Few results of the testing of the TDS facility are shown, illustrating its most important performances. The temperature of the sample is increased linearly as: $T(t) = T_0 + \beta t$, $\beta$ being the heating rate whose values can be adjusted continuously from $2\,\mathrm{Ks}^{-1}$ to $90\,\mathrm{Ks}^{-1}$. $T_0$ and $T$ can be fixed within the interval 130—1500 K.

## *1. Introduction*

Thermal desorption spectroscopy (TDS) is one of the most frequently encountered methods in the studies of the kinetics of desorption of gases adsorbed on various metallic surfaces[1]. In this paper we give a description of technical details and scientific performances of a simple ultrahigh (UHV) apparatus equipped with a TDS facility, which has been designed in our laboratory for carrying out thermal desorption measurements at temperatures ranging between the liquid nitrogen and above room temperature.

Although very simple as a technique, TDS should be designed very carefully in order to simplify the interpretation of results, and to avoid injurious influences of the surrounding surfaces as well as those arising from improperly or insufficiently controlled heating of the sample. A great deal of these problems can be avoided by using an electronically controlled and programmed temperature ramp[2]. Cooling of the sample holder appears to be of great importance but the lowest temperature required depends on the specific experiment.

## 2. *Description of the apparatus*

### 2.1. *Pumping system*

The apparatus comprises a 50 l main chamber which is presently pumped by means of two sorption pumps (roughening line), 140 l/s ion getter pump and separatelly mounted titanium sublimation pump (TSP) (Fig. 1). The TSP shield can

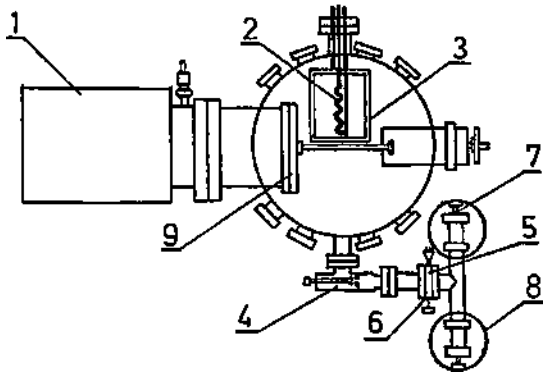


Fig. 1. Pumping system: (1)-140 l/s ion getter pump, (2)-titanium sublimation pump (TSP), (3)-shield for TSP, cooled by water or liquid nitrogen, (4)-all-metal valve, (5)-thermocouple gauge, (6)-ventvalve, (7)-sorption pump valve, (8)-sorption pump, (9)-valve separating ion pump from the main chamber.

be cooled by tap water or liquid nitrogen. When needed, ion pump is separated from the main chamber by the use of Viton sealed valve, constraining thus the baking of the system to below 180°C. The pressure is measured in the roughing line, in the main chamber, and in the ion pump. Nude ionization gauge and a quadrupole mass spectrometer (QMS) are used as pressure indicators in the main chamber, the QMS indicating total and partial pressures and serving simultaneously as a helium leak detector. Nude ionization gauge is linear in the range $10^{-2}$—$10^{-9}$ Pa. After bakeout of the ion pump and the working chamber, pressure of $5 \times 10^{-8}$ Pa has been routinelly achieved. In due course the ion pump will be replaced by 170 l/s turbopump so as to enable rapid evacuation of the main chamber after argon ion bombardement.

### 2.2. *Main chamber*

The main chamber supports eight lateral ports (Fig. 2a) occupied by (a) diode probe unit (1), (b) scanning ion gun (2), (c) quadrupole mass spectrometer (3), (d) ionization gauge (4), (e) two leak valves (5) and (7), (f) viewing port (8) and (g) double source evaporation unit (6). (a) The diode probe unit has been designed for measuring the work function caused by gas adsorption/desorption on/from the sample surface. It consists of a small chamber accomodating a linear motion drive and all necessary feedthroughs. A filament, serving as a cathode, is mounted on

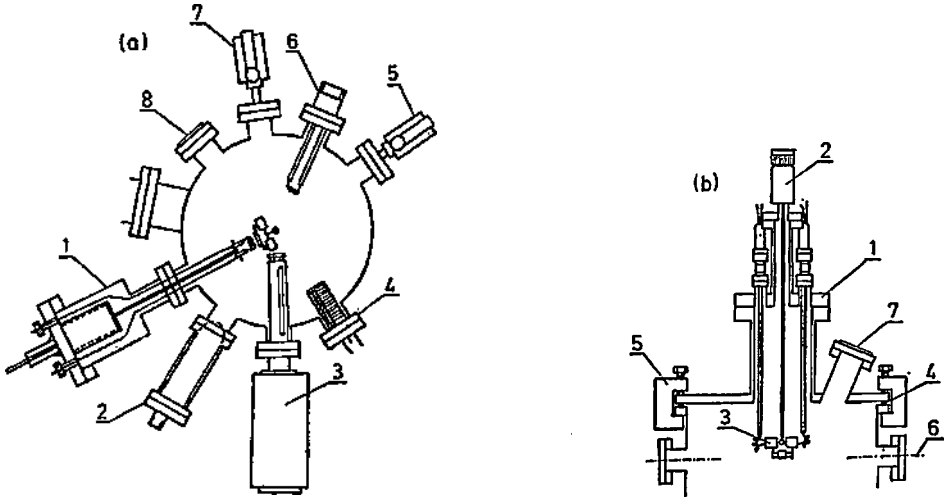


Fig. 2. a) Eight lateral ports of the main chamber: (1)-diode probe unit, (2)-ion bombardment gun, (3)-quadrupole mass spectrometer, (4)-ion gauge, (5)-leak valve, (6)-evaporation unit, (7)-leak valve, (8)-window.

b) Main flange of the working chamber with rotary drive unit: (1) 150 mm flange with six mini-flanges, only two occupied by vacuum breaks are shown and (2)-rotary drive (centered), (3)-sample holder, (4)-silver O-ring, (5)-one of 36 clamps used to press the Ag gasket, (6)-eight ports plane, (7)-window.

the linear motion drive. Such construction enables: i) simple adjustment of a diode geometry, and ii) fast removing of the filament from the sample holder when the sample, serving as the anode in the diode, is rotated towards any of the remaining ports (see Fig 2a and 2b). (b) Scanning ion bombardment gun with corresponding power supply (Varian) with beam energy variable within the 0—3 keV range. (c) Quadrupole mass spectrometer (Vacuum Generators) serves as total and partial pressure indicator (mass range 1—100 amu) and as a helium leak detector. (d) The ionization gauge is of a nude type with two tungsten filaments. (e) Two commercial fine control leak valves operating below $10^{-8}$ Pa are mounted on to two chamber ports. (f) viewing port is 36 mm dia UHV-zerolength 7056 Glass/Kovar window. (g) The double source evaporation unit (Fig. 3) consists of two separately power-supplied (25V/25A) tungsten filaments onto which a thin wire of a desired metal could be coiled and evaporated consequently. Two sources have been introduced in order to enable production of binary systems (alloys).

The sample is mounted on the rotary drive (perpendicular to the eight ports plane) in such a way that its face could be oriented towards any of the ports (Fig. 2b). All connections to the sample pass through six miniflanges mounted on the rotary drive unit. The largest flange on the apparatus (360 mm dia) is clampped to the main chamber (36 clamps) and sealed with 1 mm thick silver O-ring. All other flanges are of the Conflat type with copper gaskets.

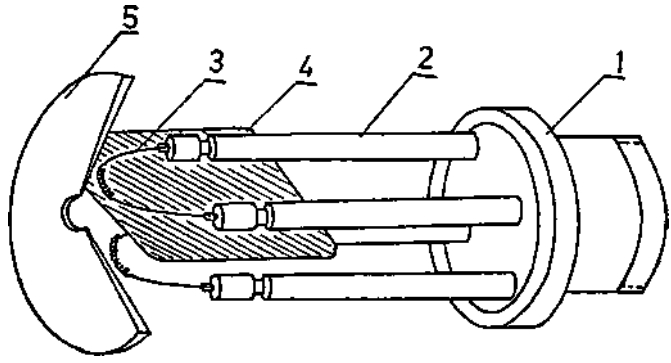


Fig. 3. Double source evaporation unit: (1)-high current feedthrough on 70 mm. Conflat flange, (2)-6 mm ø Cu rod, (3)-tungsten filament with coilled metal wire, (4)-shutter preventing sputtering on the second filament, (5)-shutter preventing sputtering on the surrounding surfaces and directing the beam towards substrate.

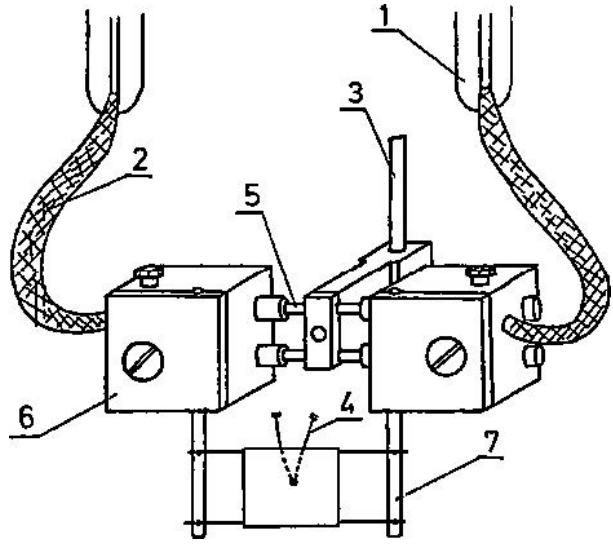


Fig. 4. Sample holder and mounting of the specimen: (1)-Cu tubes, (2)-Cu braids, (3)-connection to rotary drive, (4)-thermocouple, (5)-stainless steel rods insulated from copper block by ceramic tubes, (6)-copper block, (7)-Mo rod, (8)-specimen hanging on tungsten heaters.

### 2.3. *Sample holder*

In order to perform TDS measurements at low temperatures we designed a sample holder which would enable us to cool and to rotate the sample simultaneously. In addition to that, it was very important to mount a specimen so as to minimize the influence of the surrounding surfaces on the reading of the mass spectrometer. Fig. 4 shows the specimen holder which fulfills the above mentioned requirement[3]. The sample (usually a crystal or a foil) is spotwelded to two 0.25 mm thick tungsten wires which serve as heaters. Tungsten wires are spotwelded to two molybdenum rods (1.5 mm dia) which are fixed in copper blocks. These blocks are electrically insulated from each other and the rest of the apparatus. One liquid feedthrough is connected to each block through flexible copper braid. This construction permits free rotation of the sample. Liquid feedthroughs are made of U-shaped copper tubes soldered to the stainless steel tube which is welded onto a miniflange. A vacuum break separated the feedthrough from the rotary drive unit enabling thereby its use as a high current feedthrough. The control and measurement of the sample temperature is achieved by spotwelding Ni/Ni-Cr thermocouple onto the back side of the specimen. During the cleaning procedure the specimen is oriented towards argon ion gun at the distance of 12 cm. When oriented towards mass spectrometer analyser the distance between front face of the sample and the opening of the analyser is 2 cm.

### 2.4. *Electronics and power supply for TDS*

Accurately controlled heating of the specimen is essential for TDS experiments. The most common way to perform such an experiment is to increase the temperature of the sample according to a linear law

$$T(t) = T_0 + \beta t \tag{1}$$

$\beta$ being the heating rate. The heating rate depends firstly on the pumping speed of the gas[4] concerned, which, among other parameters, depends on the chemical activity of the gas and the type of the pump used. Therefore, one requires a very broad range of heating rates depending on the type of the experiment[5]. On the other hand, there is a broad spectrum of possible samples: monocrystals, foils, evaporated metalic films on various substrates, etc. Obviously, there is a very large range of temperatures and heating rates to be covered. This can be achieved by the use of a thermocouple controlled temperature programmer which regulates the voltage of the power supply connected to the sample (Fig. 5). Such a programmer should be optimized[2] for fast and slow response of the heating circuit and for the work with samples of various sizes. At the same time no electrical potential should occur on the sample as a consequence of the temperature measurement or heating. Based on works of Mikonis and Green[6] and Herz et al.[2] (the latter being a substantially improved version of the former) we constructed a programmer which fulfills the above mentioned requirements. The heating rate is variable over the range of 2—90 K/s, with the maximum temperature of 1500 K. It is possible to start the heating of the sample and/or to stop it at any desired temperature within the interval 130—1500 K. The programmer controls DC power supply (home made, 5V/40A with current stability of $10^{-4}$)

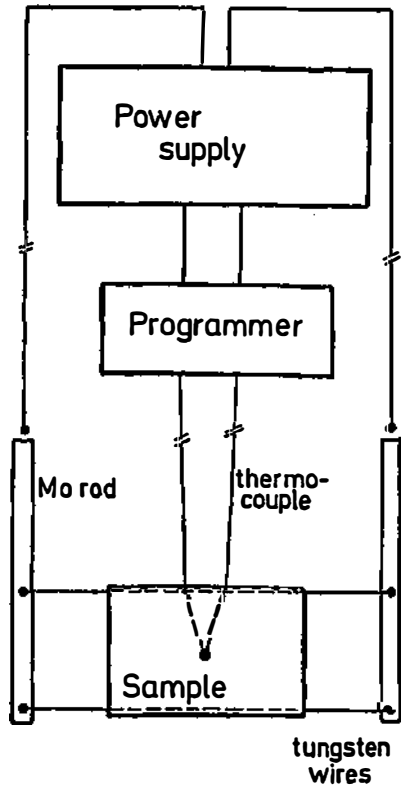


Fig. 5. Simplified scheme of the thermocouple controlled specimen heating arrangement.

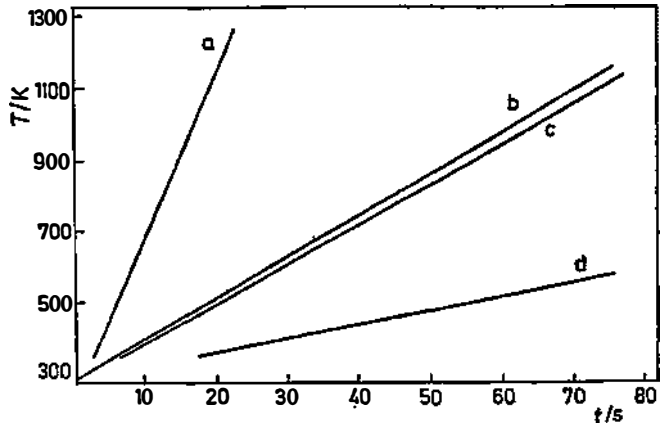


Fig. 6. Heating curves for different heating rates ($Ks^{-1}$): a) 45, b) 11, c) 10, d) 5. a, c, d — Pd sample; b-Cu sample.

## 3. *Few examples of testing*

Most of the testing of the method has been carried out on Cu (100) sample (8 × 8 × 3 mm) and polycrystalline palladium foil (10 × 10 × 0.5 mm) Fig. 6 shows $T$, $t$ diagrams for Cu (line b) and Pd (lines a, c, d) for various heating rates. One sees clearly that the temperature of the sample increases linearly. However, the linearity of the voltage ramp of the controller/programmer alone is not sufficient to achieve the linearity of the $T$, $t$ characteristics. Our experience is that the symmetrical arrangement of the specimen with respect to the heaters and the current consumed by the heaters varies during the programmed heating period. This is displayed in Fig. 7 for four different heating rates. Right at the beginning

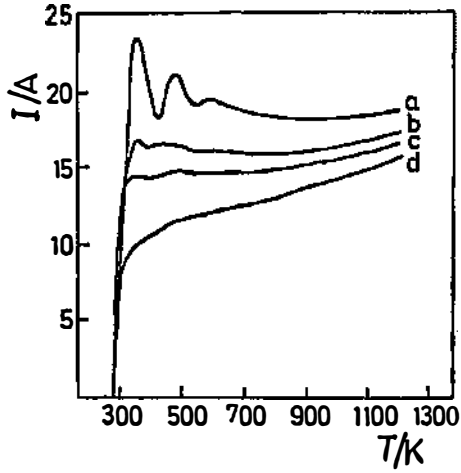


Fig. 7. I (heaters)/T curves for different heating rates ($Ks^{-1}$): a) 90 b) 45 c) 25 d) 10.

there is a sudden jump of the current. This finding is similar to that of Herz et al.[2] who gave detailed explanation for such a behaviour. For the very slow ramps (curves a, b) there is almost no oscillations in the current intensity, while very fast regulation (curves e, d) causes significant oscillations. However, the final result is, in all cases, a linear temperature increase of the specimen. $I$ ($T$) curves in Fig. 7 have been obtained for Pd (polycrystaline foil) sample. It should be pointed out that the shape of such curves is not independent on the size and kind of the specimen.

Fig. 8a shows thermal desorption spectra of CO desorbing from polycrystaline Pd foil after exposure to 10 L of oxygen (1L = $1.33\ 10^{-4}$ Pa exposure of 1 second) at two different sample temperatures. These spectra were obtained during the cleaning procedure of the Pd foil surface. The first peak (500 K) corresponds to molecular CO originating from the residual atmosphere. The second peak (900 K) originates from CO produced by oxidation of surface deposited carbon. By keeping the sample at 600 K during exposure to $O_2$ followed by cooling to 300 K, we obtained TD spectrum displayed in Fig. 8b. There is no more CO molecular peak (at 500 K) in the spectrum because all available surface sites were occupied by oxygen atoms during adsorption process.

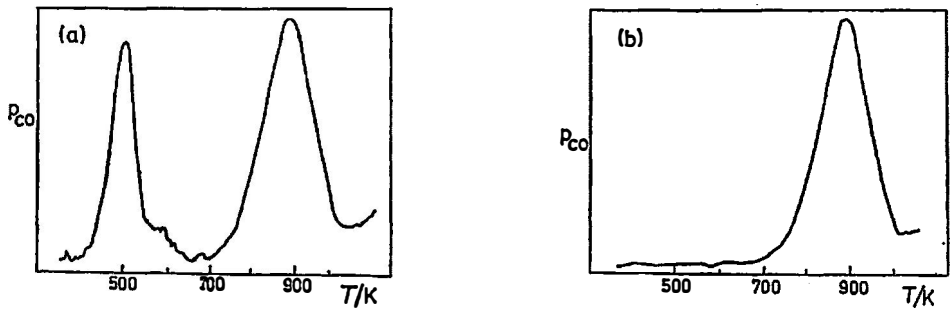


Fig. 8. TDS spectra of CO/Pd (polycrystalline foil) obtained after expossure to 10L $O_2$ at a) 300 K and b) 600 K at base pressure $5 \times 10^{-8}$ Pa.

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# ULTRAVISOKO VAKUUMSKI UREĐAJ ZA TERMALNU DESORPCIJSKU SPEKTROSKOPIJU PRI NISKIM TEMPERATURAMA

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U radu je prikazan jednostavan ultravisoko vakuumski uređaj u koji je ugrađena metoda termalne desorpcijske spektroskopije (TDS). Posebno su istaknuti najvažniji tehnički detalji uređaja i pumpnog sistema, radne komore i relevantne elektronike. Nekoliko karakterističnih rezultata testiranja uređaja ilustriraju performanse ugrađene TDS metode. Temperatura uzorka diže se linearno: $T(t) = T_0 + \beta t$, pri čemu je $\beta$ brzina grijanja. $\beta$ se može kontinuirano varirati od 2 $Ks^{-1}$ do 90 $Ks^{-1}$. $T$ i $T_0$ se mogu fiksirati na bilo kojoj vrijednosti unutar 130 K—1500 K.