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THE USE OF THERMAL ANALYSIS TO SELECT THE STANDARD OUTGASSING CONDITIONS OF A SET OF REFERENCE ADSORBENTS

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ABSTRACT

The increasing need for reference materials in the field of low surface area adsorbents (such as pigments, fillers, medicinals...) made it necessary to launch, in the scope of BCR (Bureau Communautaire de Référence, Bruxelles) a campaign for selecting and characterizing a set of 7 adsorbents (0.1 to $10 m^2 g^{-1}$). The necessary selection of standard and reproducible outgassing conditions was carried out using the method of Controlled reaction Rate Thermal Analysis (CRTA) associated with vacuum TG. The sensitivity and relevance of this method is illustrated here (especially for 2 samples loosing less than 0.03% of their initial mass up to 500°C) and the detection of small structural changes (for an alumina and a bronze) is commented on.

INTRODUCTION

As stated by S. Brunauer in his famous book on "The adsorption of gases and vapors" (ref.1), "in all adsorption measurements the first step is to obtain the surface of the adsorbent in the highest possible state of purity, i.e. to free it as completely as possible from gases already adsorbed before the beginning of the experiment". The importance of this first step is still pointed out in the recent suggestions of the IUPAC Subcommittee on reporting gas adsorption data (ref.2). In practice, this outgassing is obtained by heating either under a flow of inert gas or, more frequently, in vacuum (partly because the gas adsorption cells easily lend themselves to a vacuum operation and partly because the adsorption experiment, in most cases, must begin with a vacuum in the adsorption cell). The extent of outgassing has a direct influence (i) on the extent of the *surface area* which is actually *available* to the adsorbate (this is critical in the case of microporous samples), (ii) on the chemical nature (for instance, more or less hydroxylated) of the surface, which may have a direct influence on the *packing of the nitrogen molecules* in the monolayer (ref.3) and (iii), in any case, on the *mass of the sample* (on which depends the value of any "specific" quantity like the specific surface area). Now, partly because of the surface heterogeneity of the adsorbents of technological interest,

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outgassing usually takes place in a broad range of temperatures (very often, up to 1000°C). In these conditions, heating may have other effects than a mere outgassing : the sample may for instance undergo structural changes, sintering or migration of one component towards the surface.

The aim of selecting standard outgassing conditions is therefore to find conditions in which the sample may reach a *reproducible state* (availability of the surface to the adsorbate molecules, chemical and structural nature of the surface, overall composition) but *with the least possible modification* (otherwise, it would be a matter of pretreatment rather than of outgassing). The reproducibility must be obtained relatively easily (the temperature conditions must not be too sharp) and even in the case of variations in the conditions of storage of the sample (therefore, the temperature must be high enough to allow the desorption of those species which could have been adsorbed during storage).

CHOICE OF THE THERMOANALYTICAL PROCEDURE

The "thermal path" followed by an adsorbent during outgassing is of course a function of *time*, *temperature* and of the *partial pressure* of the gas being evolved. Drastic changes in the kinetics of outgassing may be observed even within the pressure range usually referred to as "vacuum" (ref.4). In these conditions, we found it appropriate to follow the outgassing of the reference samples by using *"vacuum" TG* but *with a strict control of the residual pressure*. Since a control of the pressure involves the control (and limitation) of the pressure gradients within the sample and since these gradients are directly depending on the rate of outgassing, an efficient way to reach our goal of highly reproducible outgassing was to associate vacuum TG and Controlled outgassing Rate Thermal Analysis (C.R.T.A.), a technique where the heating of the sample (here, in the thermobalance) is carried out in such a way that the rate of reaction (here, a rate of outgassing) is controlled (and usually kept constant) throughout the thermal analysis (ref.5). Depending on the equipment used, it happens that either as a cause or as a consequence of the constant rate of outgassing, the residual pressure is also constant. The experimental set up was previously described (ref.6).

TG RESULTS AND DISCUSSION

The TG outgassing curves obtained under a *constant* residual pressure of 2.10^{-5} torr and up to a temperature of 500-550°C are given in Fig. 1. These curves lead to the following observations :

- In the case of four samples (Quartz, Titania, Tungsten and Alumina NPL-4) a large part of outgassing takes place at room temperature and comparative experiments (not reported here) have shown us, as expected that this part was

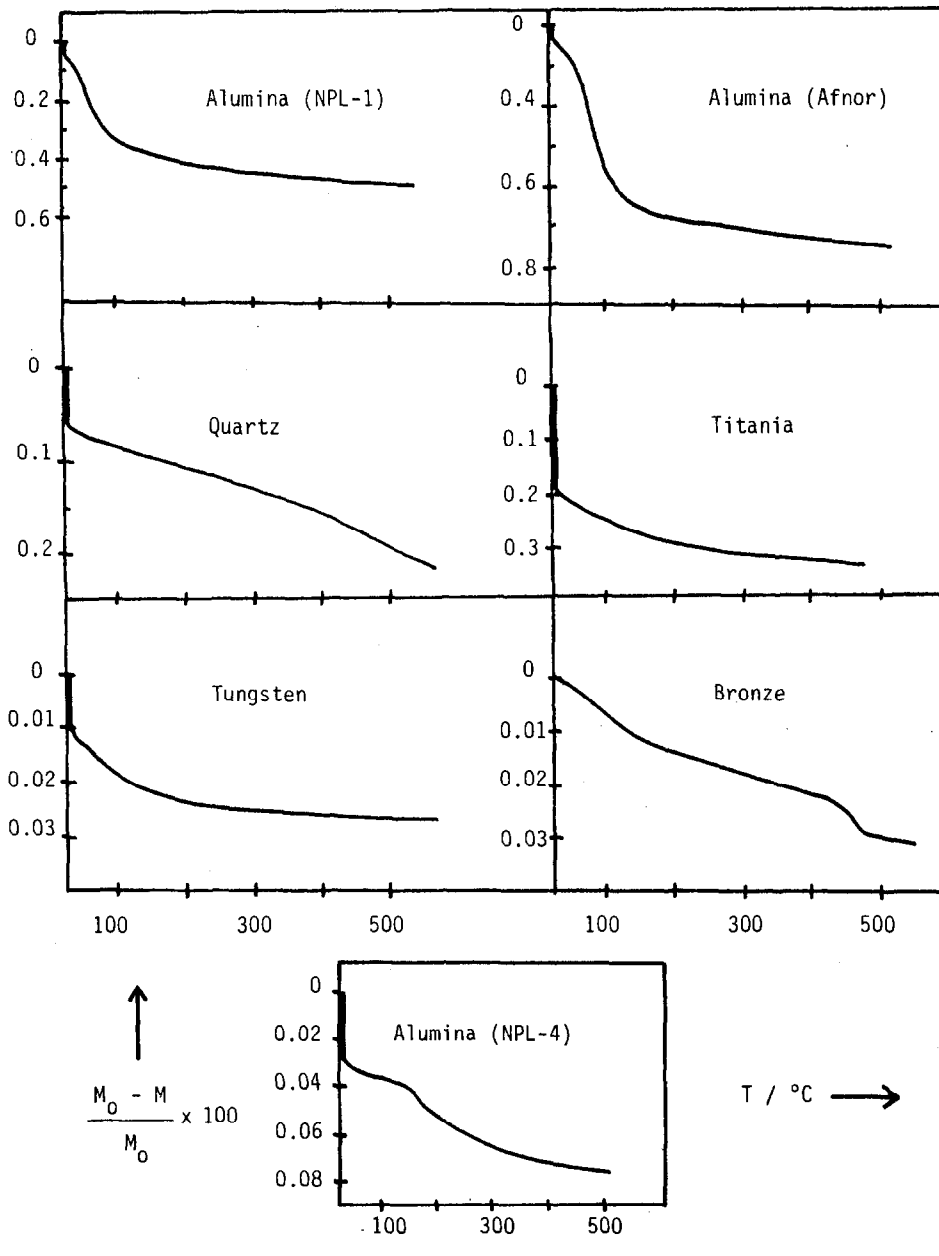

Fig. 1. TG curves of the 7 adsorbents (under controlled vacuum and rate of outgassing).

highly dependent on the storage conditions, so that the starting mass of sample is not, of course, a safe basis.

- For five samples (Alumina NPL-1, Alumina Afnor, Quatrz, Titania and Tungsten) the slope of the TG curve falls down to a comparatively small value at temperatures of c.a. 25°C (Quartz) 100°C (Alumina NPL-1) or 150°C (Alumina Afnor, Titania and Tungsten). The reproducibility in the state of the adsorbent is likely to be the highest when the dependence of the extent of outgassing on the temperature is the smallest. For the sake of simplification we may say that the often chosen outgassing temperature of 140°C under vacuum is, still here, a good choice for the 5 samples considered.
- Although the overall loss of the *Bronze* sample is of 0.03% between 25 and 525°C, the resolution of this type of TG allows to detect a significant drop around 450°C, whereas the *Alumina* NPL-4 undergoes a significant mass change around 150°C, *i.e.* exactly within the usual outgassing temperature range. For both samples it was felt necessary to have a further look to their structure and texture modifications during heating.

STRUCTURE CHANGES OF THE BRONZE AND ALUMINA NPL-4 SAMPLES

The X-ray study was carried out using the method of powders, on a CGR diffractometer with a copper anticathode. The $K\alpha_1$ radiation was isolated by means of a curved slide quartz monochromator.

The study shows that after outgassing at 140°C, the bronze contains 2 different phases (both cubical face centered) which are likely to be metastable since, after outgassing at 500°C only one new cfc phase can be found. The phenomenon detected by the TG curve around 450°C is therefore a real annealing leading to a more stable and better crystallized sample.

In the starting alumina (NPL-4) sample, at least 3 crystalline phases of the corindon type and one amorphous phase was detected. Under heating, the crystallization improves and the proportion of amorphous alumina decreases. Impurities or even occluded water may explain the existence of these various crystalline phases.

NITROGEN ADSORPTION STUDY ON THE BRONZE AND ALUMINA NPL-4 SAMPLES

Nitrogen adsorption was carried out at 77K by means of a symmetrical and automated adsorption balance described previously, using the quasi-equilibrium procedure (ref.7). Processing the data by the BET method, one obtains the results in Table I :

TABLE 1
BET specific surface areas

Sample	Outgassing temperature/°C	Specific surface area / m^2g^{-1}
Bronze	400	0.090 ± 0.005
	500	0.100 ± 0.005
Alumina NPL-4	100	0.120 ± 0.005
	200	0.121 ± 0.005

As can be seen, the very small value of the surface area does not allow to detect, by nitrogen adsorption , any significant change in the surface area of both samples. Fortunately, no sintering is observed for the bronze above 450°C. In these conditions, an outgassing temperature of 140°C may be kept for the bronze, except if the subsequent use of this sample makes it preferable to increase its stability by a previous annealing at 500°C. In the case of alumina (NPL-4) it seems wise (although not required from the nitrogen adsorption experiments) to stay apart from the 140-180°C temperature range in which a slight recrystallization is observed.

CONCLUSION

The procedure suggested for selecting "standard" outgassing conditions (i.e. conditions which need to be both safe and easy to reach) is therefore the following :

- Plot the TG outgassing curve under conditions of controlled vacuum throughout the experiment. This may be achieved by associating "vacuum" TG with Controlled outgassing Rate Thermal Analysis (CRTA).
- Look for the regions of weak slope of the curve, following the advice of the IUPAC Subcommittee on reporting gas adsorption data (ref.3).
- If 140°C is not included in these regions or if an irreversible and unwanted modification is likely to occur under 140°C, then select another outgassing temperature.

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