

## THE USE OF TGA TO ESTIMATE THE LOADING OF ORGANICS ON ACTIVATED CARBON

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### ABSTRACT

Activated carbon is used in the mining industry for the recovery of precious metals, and is used in the treatment of waste-waters for the removal of pollutants. During such applications the carbon becomes poisoned by a wide spectrum of organics of which the concentrations and identities are not usually known. A simple mass balance and TGA data can be used to calculate the loading of organics on activated carbon if the residual mass of pyrolysed organics is known; however, this information is not usually known for industrial carbons. In such cases the slope of the TGA curve for the loaded carbon heated above 850°C in an inert atmosphere may be used to estimate the loading of organics on the carbon. Different carbons loaded with phenol, benzoic acid and methylene blue, as well as carbons loaded from plant solutions, were used to verify the use of this new procedure.

### INTRODUCTION

Activated carbon (AC) has been used widely in adsorption processes for the recovery of valuable materials, the fractionation of mixtures and the removal of toxic species. The removal of organic pollutants by activated carbon from industrial and municipal waste-waters has received wide attention recently [1–3]. Since the 1970s activated carbon has also been utilized in the mining industry for the extraction of gold and silver cyanides from leached slurries [4,5]. Organic impurities poison the carbon during the adsorption cycle in a carbon-in-pulp plant and some are not removed in the elution and acid washing cycles.

The economic feasibility of most activated carbon processes is dependent on the cost of regeneration of the spent carbon. Chemical regeneration can usually restore only a fraction of the potential activity of the carbon when it has adsorbed organics from industrial solutions [6]. Although thermal regeneration has been used successfully in restoring the activity of such carbons, little fundamental work has been done to optimize operating conditions.

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It is essential to know the loading of organics on activated carbon in order to plan the cycle of thermal regeneration and to optimize the temperature, partial pressure of the oxidizing gas and time of regeneration. The loading of organics can be determined easily when adsorption takes place from solutions of known volume and composition. Unfortunately, most industrial waters contain a multitude of unidentified organics. The objective of this paper is to propose a method by which thermogravimetric analysis (TGA) could be used to estimate the loading of unidentified organics on activated carbon.

## EXPERIMENTAL

The two activated carbons used here and which were made from coconut shells were Le Carbone G210 AS, with an apparent density of  $890 \text{ kg m}^{-3}$ , and Degussa Eponit C20, with an apparent density of  $778 \text{ kg m}^{-3}$ . The extruded coal-based Norit carbon had an apparent density of  $650 \text{ kg m}^{-3}$ . All particles of the Le Carbone and the Degussa carbons were in the sieve size fraction 1.4–1.7 mm. The Norit carbon consisted of cylindrical particles with diameter 1 mm and a log-normal distribution of lengths with an average length of 3.82 mm. Two industrial samples of coconut-activated carbon were obtained from a Gencor gold mine in the Evander area in South Africa. One sample was taken after elution and acid washing, but before the regeneration stage, while the other one was taken after regeneration in a rotary kiln.

The phenol, benzoic acid and methylene blue used as adsorbates were all analytically pure and did not decompose at the drying temperature of  $120^\circ\text{C}$ . Deionized glass-distilled water was used to dissolve these adsorbates.

A sample of carbon, previously dried to a constant mass for 24 h at  $120^\circ\text{C}$ , was weighed accurately before being added to a solution of the particular adsorbate. These mixtures of carbon and solution were sealed in closed containers and agitated for three days. The sample of carbon was then removed, dried for 24 h at  $120^\circ\text{C}$  and weighed. The increase in mass was taken as the loading of the particular adsorbate on the carbon. A similar procedure was followed by Suzuki et al. [7].

A Stanton Redcroft Massflow thermobalance was used to heat samples of activated carbon in a recrystallized alumina crucible at a heating rate of  $7.6^\circ\text{C min}^{-1}$ . The masses of the carbon samples on a dried unloaded basis were: 1.3 g of gold mine samples, 1.477 g of Le Carbone, 1.480 g of Degussa and 1.470 g of Norit carbon. The loss of mass by a sample of carbon was recorded continuously during the course of temperature rise.

The argon which was used to flush the furnace was purified by passing it through a de-oxidizing unit (concentrated sulphuric acid, ascarite, calcium chloride and magnesium perchlorate). At the flow rate of argon used ( $6 \text{ cm}^3$

$s^{-1}$ ) it was found that variations in the flow rate had no significant effect on the mass loss pattern. When a sample of high grade graphite powder was heated to  $1100^{\circ}\text{C}$  no mass loss could be detected, which showed that the atmosphere in the thermobalance was inert.

## METHODS OF ESTIMATION

Various authors [7–10] have established that organics on carbon decompose during heating in an inert atmosphere to leave a carbonaceous residue in the pores of the carbon. The activity of the carbon will be restored only if this residue is oxidized by steam or carbon dioxide. Different authors have obtained different values for the fraction of residual material, even when the same adsorbate is used. Suzuki et al. [7] measured a residue of 61% of the initial mass of phenol adsorbed on a bituminous coal-based carbon, Wang and Smith [11] measured a value of 47% and Van Deventer and Camby [8] obtained a value of 32.6% for a coconut shell carbon. Furthermore, Suzuki et al. [7] showed that the fraction,  $\beta$ , of organics which remains as residue after decomposition could vary widely for different adsorbates. Therefore, it is almost impossible to a priori predict a combined value for  $\beta$  for a multitude of adsorbates in industrial solutions. However, if such a value is known, then the loading of organics on activated carbon can be calculated from the following additional information:

- (1) the initial mass of the loaded carbon,  $M$  (g);
- (2) the mass loss from the loaded carbon during linear heating in an inert atmosphere,  $Q$  (g);
- (3) the fraction mass loss from an unloaded sample of carbon during linear heating in an inert atmosphere,  $\alpha$ .

The values of  $\beta$ ,  $Q$  and  $\alpha$  should all be determined at the same temperature, above  $850^{\circ}\text{C}$ , where the rates of decomposition of the loaded and unloaded carbon are equal [8].

With  $W_0$  = initial mass of virgin carbon (grams), and  $q_0$  = initial loading of organics on carbon, an initial mass balance on the loaded carbon gives

$$W_0(1 + q_0) = M \quad (1)$$

A mass balance on the carbon after TGA gives

$$\alpha W_0 + (1 - \beta)q_0 W_0 = Q \quad (2)$$

so that

$$q_0 = \frac{Q - \alpha M}{(1 - \beta)M - Q} \quad (3)$$

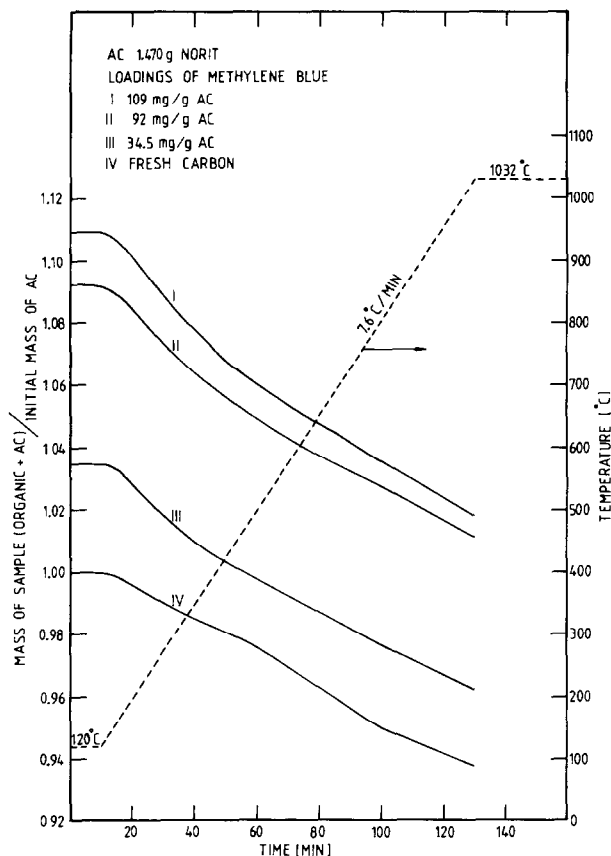


Fig. 1. TGA curves for Norit carbon having different loadings of methylene blue.

The determination of the characteristics  $\alpha$  and  $\beta$  for a single adsorbate on coconut carbon has been discussed earlier [8]. Thus with these values known,  $q_0$  could be determined easily by measuring  $Q$  in TGA. The use of TGA to estimate the loading of organics on activated carbon has not been described in the literature.

If the value of  $\beta$  cannot be measured, then the slope of the last part of the TGA could be used to estimate a value for  $q_0$ . As required in the previous method, the TGA behaviour of the unloaded carbon is also used in the method described subsequently.

Figures 1–4 show TGA curves for the carbons loaded from synthetic solutions. These curves were found to be reasonably reproducible. Figure 1 shows that the curves for methylene blue are very similar in shape regardless of the initial loading. Similar behaviour has been observed for phenol [8]. However, Figs. 2–4 show that there are significant differences in the shapes of the TGA curves for phenol, methylene blue and benzoic acid. In every

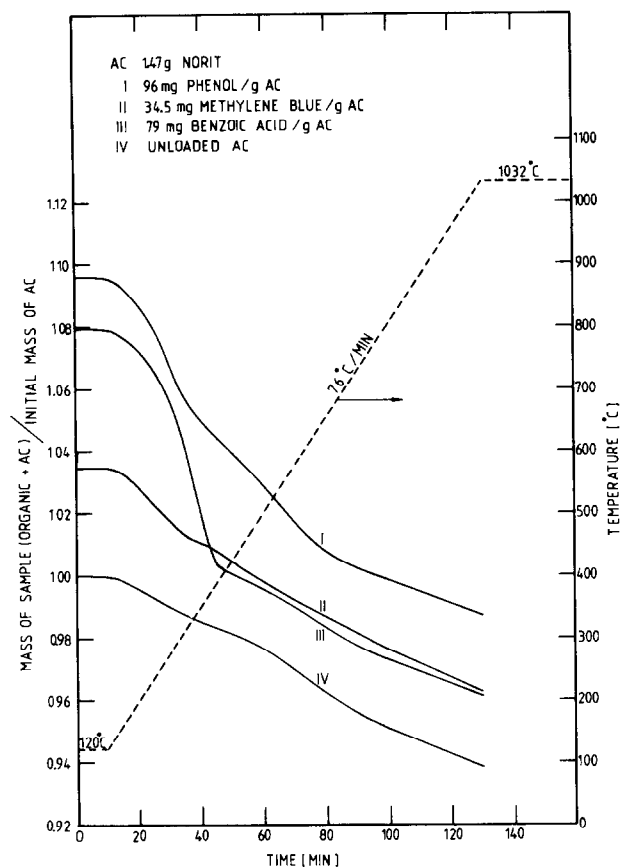


Fig. 2. TGA curves for Norit carbon loaded with phenol, methylene blue and benzoic acid.

instance methylene blue decomposed very slowly, while benzoic acid pyrolysed faster than phenol. According to Table 1,  $\beta$  for methylene blue is significantly higher than that for either phenol or benzoic acid for each carbon. Furthermore, there are significant differences between the  $\beta$  values obtained on the different carbons for each adsorbate. This may be explained by the possible influence of different pore size distributions and chemical compositions of the carbons. Suzuki et al. [7] observed different TGA curves for carbons with different macro-pore size distributions.

Figures 1–4 reveal that all three types of virgin carbon decreased about 6% in mass when heated to 1032°C. Various investigators [7–10] have observed a similar decomposition of the virgin carbon during TGA. Decomposition of the virgin carbon occurred at all temperatures between 120 and 1032°C. It is noteworthy that the TGA curves in Figs. 1–4 appear to be more or less parallel and are almost straight lines between 800 and 1032°C. Table 1 gives the slopes for these sections of the various TGA curves. The

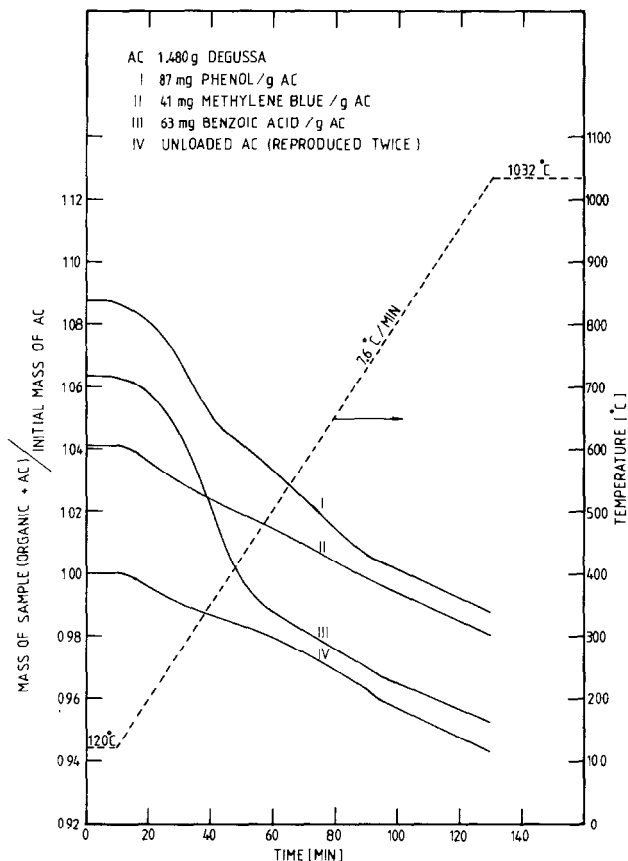


Fig. 3. TGA curves for Degussa carbon loaded with phenol, methylene blue and benzoic acid.

average slopes for the three carbons were:

$$\text{Norit: } \frac{-1}{W_0} \frac{dW}{dt} = 0.486 \pm 16\% \text{ (mg g}^{-1} \text{ min}^{-1}\text{)} \quad (4)$$

$$\text{Degussa: } \frac{-1}{W_0} \frac{dW}{dt} = 0.467 \pm 5.1\% \text{ (mg g}^{-1} \text{ min}^{-1}\text{)} \quad (5)$$

$$\text{Le Carbone: } \frac{-1}{W_0} \frac{dW}{dt} = 0.287 \pm 4.9\% \text{ (mg g}^{-1} \text{ min}^{-1}\text{)} \quad (6)$$

These slopes suggest that the decomposition of the loaded carbon above 800°C was mostly the result of decomposition of the virgin carbon only. The residue left by pyrolysis of the adsorbed organics did not decompose significantly at these high temperatures. Few authors [8,9] have noticed similar behaviour during TGA, probably because TGA was usually terminated at 800°C.

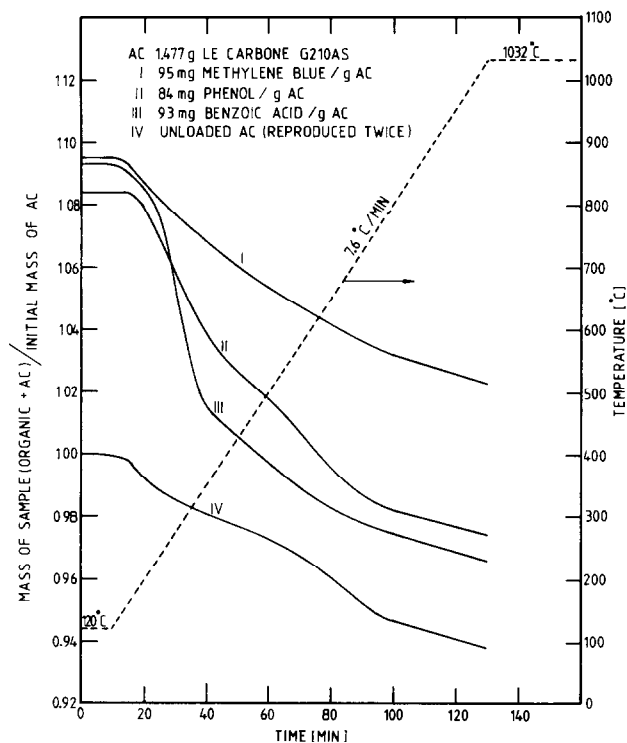


Fig. 4. TGA curves for Le Carbone carbon loaded with phenol, methylene blue and benzoic acid.

TABLE 1

Summary of TGA data for different adsorbates and activated carbons ( $W$  = mass of virgin carbon at time  $t$  for  $800^{\circ}\text{C} < T < 1032^{\circ}\text{C}$ )

Carbon	Adsorbate	$q_0$ ( $\text{mg g}^{-1}$ )	$\left. \frac{-1}{W_0} \frac{dW}{dt} \right _{T > 800^{\circ}\text{C}}$ ( $\text{mg g}^{-1} \text{min}^{-1}$ )	$\beta$
Norit	—	—	0.470	—
Norit	Methylene blue	34.5	0.498	0.696
Norit	Methylene blue	92	0.533	0.794
Norit	Methylene blue	109	0.567	0.734
Norit	Phenol	96	0.433	0.510
Norit	Benzoic acid	79	0.417	0.291
Degussa	—	—	0.500	—
Degussa	Benzoic acid	63	0.433	0.159
Degussa	Methylene blue	41	0.467	0.926
Degussa	Phenol	87	0.467	0.523
Le Carbone	—	—	0.300	—
Le Carbone	Benzoic acid	93	0.283	0.301
Le Carbone	Phenol	84	0.266	0.429
Le Carbone	Methylene blue	95	0.300	0.889

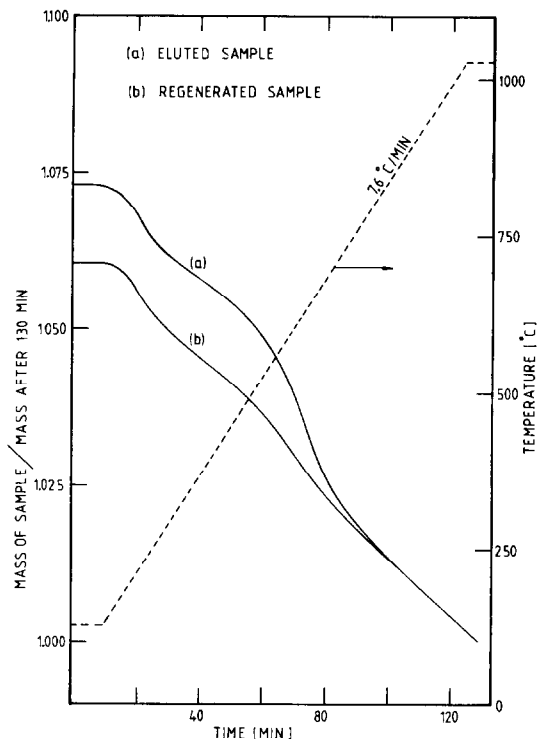


Fig. 5. TGA curves for eluted and regenerated gold mine samples of activated carbon.

Figure 5 shows similar behaviour during TGA of eluted and regenerated mine samples. As a concomitant sample of virgin carbon was not available, the mass of a sample during TGA was rendered dimensionless by dividing by the mass after 130 min. The eluted sample lost more mass than the regenerated sample, as could be expected. Both samples yielded the same mass after 130 min of TGA. The fact that both TGA curves coincide after 100 min or 800°C provides further evidence that decomposition after 800°C is caused by decomposition of the virgin carbon only.

During the manufacture of activated carbon most of the original organic substance is transformed into a hexagonal lattice of carbon. However, this transformation is seldom complete and residual hydrocarbon chains and rings remain which may cement the crystallites into clusters [12]. Some of the hydrogen bound in this way can only be removed at temperatures higher than 950°C [12]. Although the decrease in mass of virgin carbon below 800°C during TGA may be caused by pyrolysis of adsorbed impurities, the loss of mass after 800°C in an inert atmosphere can only be the result of decomposition of the active groups.

The TGA curve for virgin carbon should flatten out at temperatures higher than 1032°C. Nevertheless, Figs. 1–5 and eqns. (4)–(6) indicate that



the decomposition of virgin carbon or loaded carbon at temperatures between 800 and 1032°C may be approximated by zero-order kinetics:

$$-\frac{1}{W_0} \frac{dW}{dt} = k \quad (7)$$

where  $k$  is a rate constant which is dependent on the heating rate. It is difficult to estimate  $k$  accurately from TGA data, and a large standard deviation may sometimes be encountered, as in eqn. (4). Even though this method is not entirely accurate, it will give a first approximation of the loading on the carbon if no information is available about the adsorbate. If  $k$  is known for a virgin carbon and  $-dW/dt$  could be measured during TGA on a loaded carbon, then  $W_0$  could be calculated from eqn. (7), and  $q_0$  could be calculated from eqn. (1).

## CONCLUSIONS

(1) TGA curves for an organic adsorbed on a specific carbon were very similar in shape regardless of the initial loading. However, these curves differed for different types of carbon.

(2) There were significant differences in the shapes of the TGA curves for different adsorbates.

(3) Decomposition of the virgin carbon occurred at all temperatures between 120 and 1032°C.

(4) The TGA curves for both virgin and loaded activated carbons between 800 and 1032°C appeared to follow zero-order kinetics and were almost parallel.

(5) Decomposition of loaded carbon between 800 and 1032°C was caused by decomposition of the base virgin carbon only.

(6) A simple mass balance and TGA data for loaded and virgin carbon could be used to estimate  $q_0$  when the value for  $\beta$  is known.

(7) When the value for  $\beta$  is not known, the slopes of the TGA curves between 800 and 1032°C for loaded and virgin carbon could be used to estimate  $q_0$ .

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