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PREPARATION OF VERY PURE ACTIVE CARBON

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H.A. van der SLOOT

D. HOEDE

J. ZONDERHUIS

C. MEIJER

Netherlands Energy Research Foundation

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Netherlands Energy Research Foundation ECN

P.O. Box 1

1755 ZG Petten (NH)

The Netherlands

Telephone (0)2246 - 6262

Telex 57211

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Summary

H.A. van der Sloot, D. Hoede, J. Zonderhuis, Chr. Meijer

Preparation of very pure active carbon.

The preparation of very pure active carbon is described.

Starting from polyvinylidene chloride active carbon is prepared by carbonization in a nitrogen atmosphere, grinding, sieving and activation of the powder fraction with CO₂ at 950 ° to ~ 50 % burn-off.

The concentrations of trace and major elements are reduced to the ppb and ppm level, respectively. In the present set-up 100 g of carbon grains and ~ 50 g of active carbon powder can be produced weekly.

Keywords

Activated carbon

Impurities

Elements

Powders

Purification

Multi-element analysis

Chemical preparation

Trace amounts

Radiometric analysis

1. Introduction

Apart from its use in all kinds of purification processes [1] active carbon proved to be a very useful analytical tool in radiochemical analysis. It has been applied for:

- the preconcentration of trace elements from water [2-6], which requires carbon powder with prevailing meso-(20-200 Å) and macropores (> 200 Å) [7,8].
- the collection of volatile components (e.g. mercury, chlorinated organics) from ambient air [9]. This application requires carbon grains with a large surface area and prevailing micropores (< 20 Å).
- the preparation of standards in neutron activation analysis. The carbon grains (non-activated) are used as support. The advantage of standards prepared by pipetting aliquots of standard solutions on carbon instead of Al-foil or polythene capsules, is the possibility to obtain the same geometry for samples and standards. This is of great importance during both irradiation and measurement.

In all applications mentioned the purity of the carbon is of prime importance. Commercially available carbons are not qualified. First of all because the starting material is not pure enough and secondly because the carbonization and activation are usually carried out in stainless steel vessels.

In this work the preparation of very pure active carbon from polyvinylidene chloride is described. The carbonization is carried out in quartz vessels, the activation in a very pure aluminum oxide tube.

2. The preparation of active carbon

2.1. Raw material

Saccharose, polyvinylchloride and polyvinylidene chloride have been tested as starting material for the carbon production. From these preliminary studies one special type of PVDC, a Solvay product, proved to be useful on account of its purity and mechanical properties.

2.2. Carbonization

The procedure is:

- 250 g of PVDC is transferred to the quartz carbonization vessel (see fig.1) and the system is flushed for 15 minutes with purified nitrogen (1 l.min^{-1});
- the nitrogen flow-rate is reduced to 0.15 l.min^{-1} and the temperature controller is switched on. The temperature versus time curve shown in figure 3 is followed. In the first part the material is heated at a rate of $1 - 2^\circ$ per minute to $\sim 200^\circ \text{C}$. This temperature is maintained for one hour and then the material is heated at $2 - 3^\circ$ per minute to 800°C . Again this temperature is kept constant for one hour and the oven is switched off. (Usually the carbonization is run overnight).
- The carbonized material is split into big lumps before grinding and sieving.

The slow raising of the temperature from $25 - 200^\circ \text{C}$ is important because a rapidly increasing temperature will cause melting and strong foaming of the polymer [10]. The size of the carbonization vessel is a limiting factor in this respect.

During the carbonization of PVDC HCl is evolved which is neutralized with NaOH in a column filled with glass beads (see figure 1).

The yield of the carbonization step is $21 \pm 1\%$ of the original weight.

- After 5 - 6 hours the burn-off is measured by weighing the tube and thus the net weight of the activated carbon is obtained. The burn-off should be ~ 50 %.
- When the quality control test of the carbon (see section 3) is negative the material has to be activated under the same conditions for another 1 - 2 hours until it meets the quality standard.

3. Quality control

3.1. Adsorption properties

A carbon burned off to 50 % does not necessarily have good adsorbing properties. An additional quality control test has to be performed. It was found that the frequently applied methylene blue and iodine adsorption tests are not reliable. Therefore, a special quality control test was developed for carbons to be used for adsorption from water. It is based on the adsorption of Mn(II) from seawater using ammonium pyrrolidine dithiocarbamate (APDC) as the complexing agent. The adsorption of the Mn-APDC complex on active carbon is very critical compared to many other metal complexes. So a carbon which passes this Mn-test, is qualified for adsorption/preconcentration of many other elements.

A correlation between dye adsorption and the Mn-adsorption test could not be obtained as a high specific surface area does not guarantee proper adsorption of trace elements from water.

The adsorption test proceeds as follows:

- A sample of 100 ml seawater is filtered over a 0.45 µm filter and transferred to a beaker of 150 ml. An aliquot of a carrier-free ⁵⁴Mn⁺⁺-tracer solution is added and the solution is stirred. Then 25 mg of ammonium pyrrolidine dithiocarbamate (APDC) is added. The pH of the sample is adjusted to 7 - 8.5.
- A membrane filter (Ø 30 mm, pores 8 µm) is placed in a filtration unit (Sartorius SM 16306) mounted on a suction flask. The filter is covered with 50 mg of the carbon to be tested. The carbon is therefore suspended in 5 - 10 ml distilled water and transferred to the filtration unit. Suction is applied to form a homogeneous carbon layer on the filter.

- The sample is passed through the carbon layer. The filter is washed with two 5 ml portions of distilled water containing 5 mg APDC per 100 ml.
- The carbon covered filter is transferred to a testtube and counted together with an aliquot of the ^{54}Mn -tracer solution in a 3 x 3 - inch NaI well-type detector connected to a single-channel analyzer.
- The adsorption yield is calculated. If it is smaller than 95 %, a reactivation as mentioned in section 2.4 is necessary.

4. Purity of active carbon

The purity of several brands of active carbon has been tested by instrumental neutron activation analysis. For comparison commercial products were analysed simultaneously.

Short (1 min) and long irradiations (24 hours) were carried out at high neutron flux ($5 \times 10^{13} \text{ n. cm}^{-2} \text{ s}^{-1}$). The carbon samples were measured on a Ge/Li detector after different decay times. The elemental concentrations measured are given in table I.

The trace element levels in the "ACP" carbon are low in comparison with other carbons [17]. In particular the concentrations of the major elements are reduced considerably.

The quality control procedure for carbon purity consists of a short irradiation in a high neutron flux (1 min at $5 \times 10^{13} \text{ n cm}^{-2} \text{ s}^{-1}$). The elements Al, Cl, Na, Mn, and V are measured giving an overall impression of the impurity level. If the concentration of any of these elements exceeds the following limits:

Na	10 $\mu\text{g.g}^{-1}$
Cl	20 "
Al	20 "
V	0.05 "
Mn	0.2 "

an additional washing procedure is started using 2 N HNO_3 .

The carbon (50 g) is washed with 100 ml 2 N HNO_3 for 2 hours to remove impurities and then washed with distilled water until the pH of the washing water is 3.5 - 4.

Conclusion

The purity of the carbon obtained in this work is satisfactory for many applications. Some difficulties may be encountered in trace analysis of Cr and Al, as the blank is not negligible in these cases [15].

Three types of carbon are produced:

<u>Code</u>	<u>Description</u>	<u>Application</u>
ACP	Active carbon powder	Water analysis, Biological material
ACG	Active carbon grains	Air sampling
CG	Carbon grains	Standards for (I)NAA.

As far as water analysis is concerned the procedures developed are not limited to neutron activation techniques. X-ray fluorescence can also be applied. After desorption from the carbon using an acid digestion in a pressure-destruction vessel quantitative recovery of adsorbed elements is feasible, thus reducing the matrix influence considerably, which is of interest for the application of atomic absorption by either flame or flameless techniques.

In the collection of gases (Hg, organochlorides e.o.) from air it is now possible to eliminate the separation of collected elements which was often necessary after irradiation to eliminate the matrix activity of the collector.

The standards on carbon prepared for routine activation analysis are mixtures of a few non-interfering elements. In this way the total number of standards (capsules) to be taken along the analysis is reduced considerably. Up to now five mixtures have been prepared covering 90 % of the need in activation analysis.

Table I Trace element concentrations in different (active) carbons
All concentrations in $\mu\text{g}\cdot\text{g}^{-1}$

Element	ACP	Aktiv Kohle 2186 (Merck)	Saccharose carbon
Ag	$\leq 0,01$	-	0,012
Al	10	1,13	1,6
As	0,02	0,3	0,045
Ba	0,5	-	$\leq 0,2$
Br	0,1	0,45	0,013
Ce	$\leq 0,005$	-	$\leq 0,005$
Cd	0,5	-	-
Cl	12	50	1,5
Co	0,039	2,45	0,050
Cr	1,1	5,5	0,95
Cs	$\leq 0,002$	-	0,014
Cu	1,5	43	1,2
Eu	0,0008	-	0,0015
Fe	3,5	190	15,7
La	0,004	-	-
Lu	$\leq 0,0001$	-	0,0001
Mn	0,04	60	0,1
Na	3	80	4,6
Ni	$< 0,5$	-	$< 0,5$
Rb	$< 0,04$	-	0,07
Sb	0,15	0,8	0,012
Sc	0,0003	0,034	0,003
Se	$\leq 0,01$	0,05	0,01
Sm	0,01	-	-
Sn	$\leq 0,05$	-	-
V	0,02	0,29	0,008
Zn	0,85	14	0,51
Yb	$\leq 0,0005$	-	$\leq 0,0005$
Au	0,002	0,38	0,011
Hg	0,001	0,2	-
Hf	0,008	-	0,007
U	0,13	-	-
W	0,04	-	-

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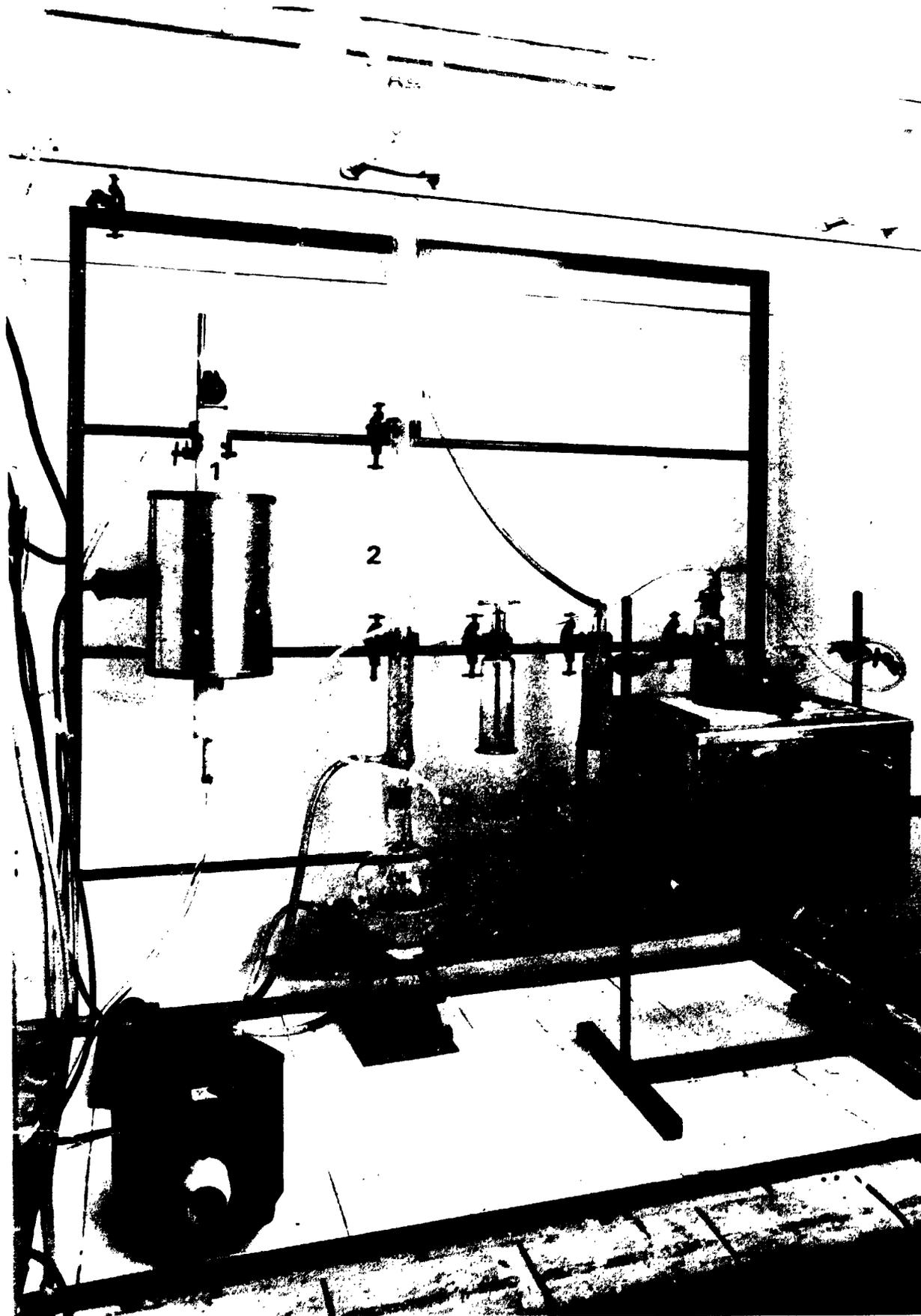


Fig. 1 Apparatus for carbonization of polyvinylidene chloride and CO_2 activation of carbon.
1. Al_2O_3 -activation tube
2. Column for neutralization of HCl.

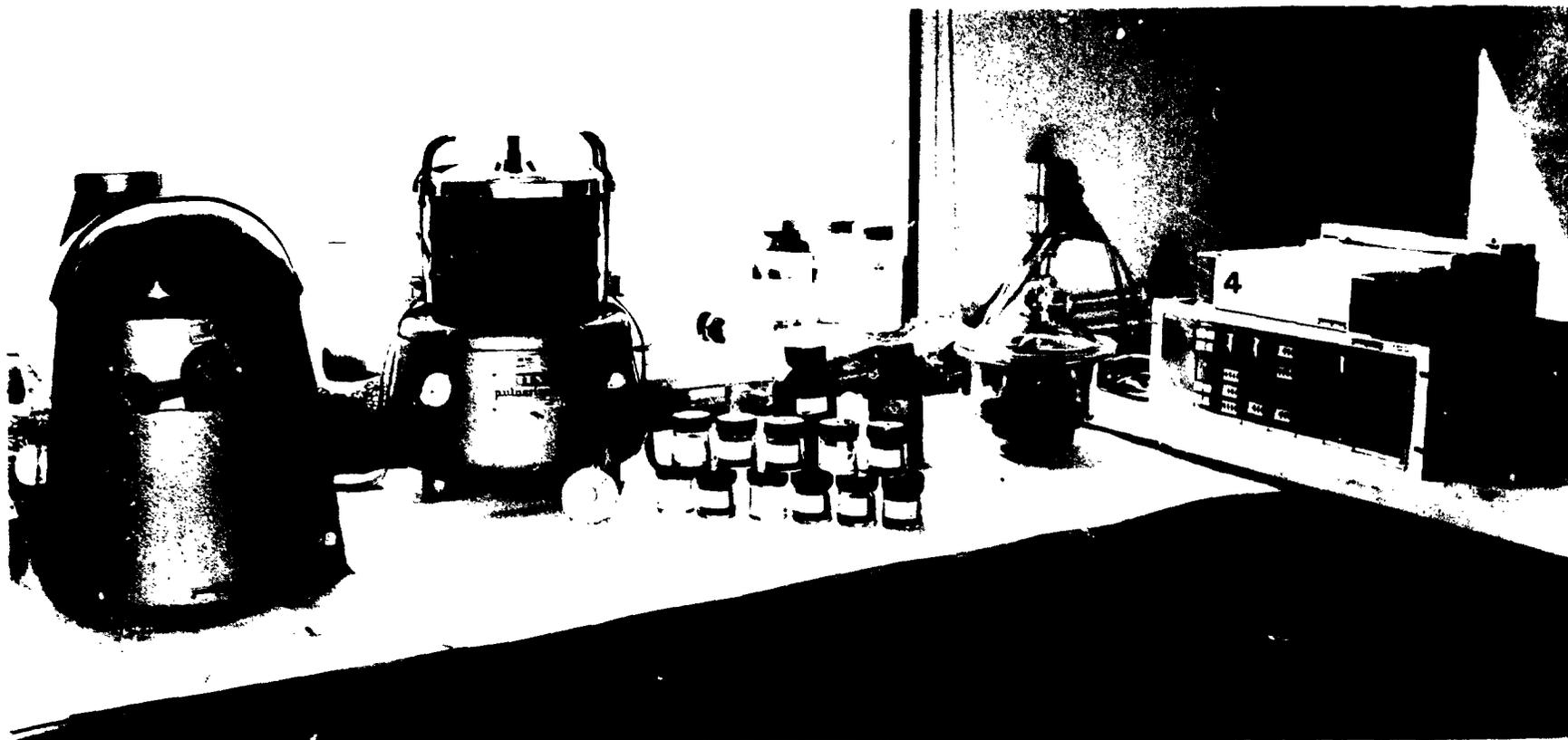


Fig. 2 Apparatus for grinding (1), and sieving (2) of carbon. Electronic equipment : Temperature controller (3) and plotter (4).

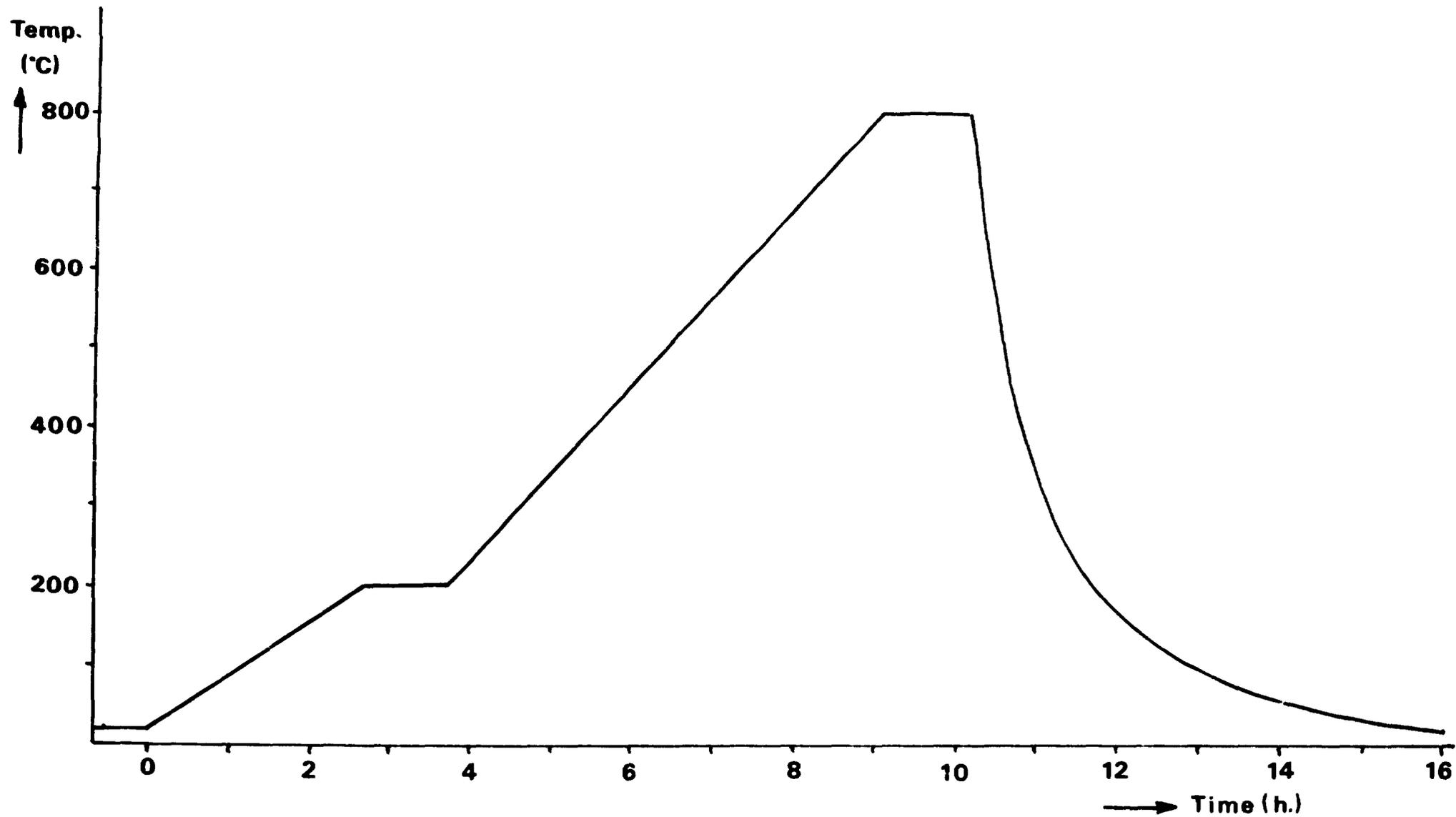


Fig. 3 The temperature versus time curve for the carbonization.