

JAERI-M

7 2 2 3

STUDY ON POROSITY OF NUCLEAR GRAPHITE BY  
ACTIVATION ANALYSIS AND MASS-SPECTROMETRY

August 1977

Motokuni ETO, Yasuichi SASAKI, Misao OUCHI and  
Nori TAMURA

この報告書は、日本原子力研究所が **JAERI-M** レポートとして、不定期に刊行している研究報告書です。入手、複製などのお問い合わせは、日本原子力研究所技術情報部（茨城県那珂郡東海村）あて、お申しこしてください。

JAERI-M reports, issued irregularly, describe the results of research works carried out in JAERI. Inquiries about the availability of reports and their reproduction should be addressed to Division of Technical Information, Japan Atomic Energy Research Institute, Tokai-mura, Naka-gun, Ibaraki-ken, Japan.

Study on Porosity of Nuclear Graphite by Activation  
Analysis and Mass-Spectrometry

Motokuni ETO, Yasuichi SASAKI, Misao OUCHI<sup>†</sup>  
and Nori TAMURA<sup>‡</sup>

Division of Nuclear Fuel Research, Tokai Research  
Establishment, JAERI

( Received July 22, 1977 )

A new method is presented of measuring porosity and pore structure of nuclear graphites. Argon content in the pores of graphite is measured by activation analysis using the nuclear reaction  $^{40}\text{Ar}(n, \gamma) ^{41}\text{Ar}$ , while composition of the gas released from it is revealed by mass-spectrometry. The porosities of SMI-24 and 7477PT graphites were calculated from the argon content and the volume ratio of argon to total gas released. For SMI-24 containing large quantity of argon, the method is effective for porosity measurement. Argon content in 7477PT is too small for the measurement.

The effect of heat treatment in a vacuum on argon content of the graphites was studied in relation of the proportion of open pore volume to total pore volume. Comparison of the results by activation analysis with those by mercury porosimetry for SMI-24 graphite showed about 55% open and 30% closed pores of the total porosity. The rest 15% is possibly crystalline distortions and defects, for which none of the methods tested are effective.

Keywords : Nuclear Graphite, Porosity, Pore Structure, Activation  
Analysis, Mass-Spectrometry, Argon Content.

---

+) Division of Chemistry, Tokai Research Establishment,  
JAERI

放射化分析および質量分析法を用いた原子炉用黒鉛の多孔性に関する研究

日本原子力研究所東海研究所燃料工学部

衛藤基邦 ・ 佐々木泰一

大内 操<sup>+</sup> ・ 田 村 則<sup>+</sup>

(1977年7月22日受理)

原子炉用黒鉛の多孔度および空隙構造の測定に関して放射化分析および質量分析法を用いた新方法を試みた結果を報告した。すなわち、黒鉛の空隙中のアルゴン量を $^{40}\text{Ar}(n, r)^{41}\text{Ar}$ なる核反応を利用して定量するとともに気体質量分析によって空隙中気体に占めるアルゴンの比率を測定し、両者を比較して空隙の体積を推算した。試料としては主としてSMI-24および7477PT黒鉛を用いた。アルゴン含量の多いSMI-24では本方法によって多孔度に関する知見が得られるが、後者ではアルゴン含量が少ないため、多孔度の計算に大きな誤差が伴うことが明らかになった。また、真空中熱処理に伴う試料中のアルゴン減少を放射化分析により測定し、水銀ポロシメトリの結果をも参照することによって、理論密度と見掛密度から計算される空隙量(試料体積の約20%)の内、約55%、30%が各々開空孔、閉空孔に対応し残り約15%がここで用いたいずれの方法によっても捉えられない微細空隙であると推論した。

---

+) 日本原子力研究所東海研究所化学部

## Contents

|  |    |
|--|----|
| 1. Introduction .....  | 1  |
| 2. Experimental Procedures .....   | 2  |
| 2.1 Measurement of Ar by means of activation analysis .....                                      | 2  |
| 2.2 Measurement of composition and volume of released gas by<br>means of mass-spectrometry ..... | 3  |
| 3. Results and Discussion .....  | 3  |
| 3.1 Activation analysis .....  | 3  |
| 3.2 Gas mass-spectrometry .....  | 5  |
| 3.3 Calculation of porosity by means of activation analysis and<br>mass-spectrometry .....       | 7  |
| 4. Conclusions .....   | 9  |
| Acknowledgements .....   | 10 |
| References .....   | 10 |

## 1. Introduction

It is well-known that most of the properties of poly-graphite are strongly affected by the porosity and pore size distribution of the material<sup>1,2)</sup>. So far, measurements of the porosity and pore size distribution have been mainly carried out by use of mercury porosimetry, butanol immersion method etc. Here, the results are reported on experiments concerning a new approach for acquiring knowledge of porosity and pore structure of graphite.

The idea adopted here is as follows. First, the content of argon (Ar) in the pores is measured by means of activation analysis, and secondly gas mass-spectrometry is carried out in order to clarify the composition of gas in the open pores and to evaluate the ratio of argon volume to the total gas volume. After that, the results of measurements of both argon content and the ratio described above are compared with each other in order to estimate the porosity. The possibility of general application of activation and mass-spectrometric techniques to the study of porosity is also discussed in this report. Champlin<sup>3)</sup> has already proposed a method for analyzing the void space of a variety of objects by use of neutron-irradiated argon in air. However, it seems to us that he rather emphasized the possibility of the application of activation technique to this field than made his experiments on an actual material very extensive. The method proposed by Champlin does require that air should be present in the sample to be investigated, and that the composition of the air is the same as that of the atmosphere from which the standards are made. In the present investigation composition and volume of gas in the pores will be measured by means of gas mass-spectrometry. Though there have been a several investigations of gas release at higher temperatures or gas adsorption to graphite<sup>4,5)</sup>, few studies have been made on the gas released from the pores at room temperature, probably because of some experimental difficulties. For example, it is very difficult to exclude the contribution of atmosphere around specimen to the results of mass-spectrometry.

In addition to these experiments described above, effect of heat treatment in a vacuum on the content of argon will also be investigated by means of activation analysis for estimating the ratio of volume of open pores to the total pore volume.

## 2. Experimental Procedures

Materials used were three kinds of nuclear graphites, i.e. SML-24, 7477PT and H327. Some properties of these graphites are shown in Table 1. Specimens 8 to 11 mm in diameter and 15 to 25 mm in length were cut from each graphite block for both the activation analysis and mass-spectrometry. Longitudinal direction of the specimens was parallel to the axis of moulding or extrusion. Some of the specimens for activation experiments were washed in acetone or trichloroethylene in order to investigate the effect of washing treatment on the argon content. Washing treatment was carried out as follows. First, specimens were washed in acetone or trichloroethylene using ultrasonic wave for about ten minutes, and after that they were dried using a rotary pump for about five hours and stored in the atmosphere for a night.

### 2.1 Measurement of Ar by means of activation analysis

Specimens were sealed in polyethylene pouches or silica tubes after measuring their weight and dimensions. Air (0.1 to 0.5 ml) sealed in four polyethylene tubes was used as a standard for the measurement of Ar content. After irradiation and carrying out  $\gamma$ -spectrometry for each air sample, volume of air in the tubes, i.e. volume of the tubes was calculated from the weight of water injected to them by use of an injector. A value of 0.933 vol.% was chosen for the composition of argon in air<sup>6)</sup>. These tubes and the specimens were irradiated in the same capsule in the pneumatic system of the JRR-2 for 5 min or in the T-pipe of the JRR-4 for 10 min.  $\gamma$ -ray spectrometry was carried out using a Ge(Li) detector (ORTEC WIN 15) connected with 4096 channel PHA (ORTEC 6420). Specimens irradiated were transferred into new pouches of polyethylene before measuring  $\gamma$ -activity. For each measurement, specimens and the standards were placed in the same geometry in relation to the detector. The value of argon content in a specimen was obtained by comparing the content of  $^{41}\text{Ar}$  produced by irradiation with that in the standards, where the  $^{41}\text{Ar}$  content was calculated from the area of  $^{41}\text{Ar}$  peak at 1293 keV with necessary correction for the half-life. After the argon content was measured for as-irradiated specimen, it was heat-treated in a vacuum in order to release Ar present in open pores. Schematic diagram of the apparatus used for the experiment is shown in Fig. 1. Main parts of the apparatus was kept in a draft chamber. Heat treatments were done at

temperatures about 110, 250 and 450°C for 30 min. The temperature was controlled within  $\pm 10^\circ\text{C}$ . The specimen heat-treated was transferred into a new pouch after it was cooled in the atmosphere, and its Ar content was measured in a manner similar to that described above.

Some specimens of SML-24 or 7477PT were stored in air of 1 atm for 24 hours after they were kept in a vacuum of  $3-4 \times 10^{-5}$  Torr for 7.5 hours. These specimens, which were believed to receive the same pre-treatment, were sealed in silica tubes for activation experiments or were used for mass-spectrometry described below.

## 2.2 Measurements of composition and volume of released gas by means of mass-spectrometry

### 2.2.1 The composition of gas

A Varion Mat CH7 mass-spectrometer was used for analyzing the composition of gas released from SML-24 and 7477PT. Specimen was placed in a glass specimen tube with a tap and connected to the gas inlet system of the mass-spectrometer. After cooling the specimen tube in liquid nitrogen bath the specimen was evacuated by opening the tap to  $10^{-4}$  Torr. Then, after the tap was closed and cooling ceased, the gas released from specimen was diffused to the reservoir of the inlet system and derived to the ion source. The detailed experimental conditions for these measurements will be described in Section 3.

### 2.2.2 The volume of gases

An Atlas CH4 mass-spectrometer was used in order to measure the volume of gases released from specimen. Gas pressure in the reservoir and peak height of each gas were measured to calculate both the total volume of the released gas and the volume of each constituent gas. The detailed experimental conditions will also be shown in Section 3.

## 3. Results and Discussion

### 3.1 Activation analysis

Figure 2 shows an example of the results obtained for the air volume standards. The linear relationship between activity and air volume indicates that such standardization is adequate for the present experiments.



Effect of washing treatment before irradiation on the content of argon in graphite is shown in Table 2. The data show that decrease in the argon content is caused by washing treatments. The amount of the decrease is larger in the case of the specimen washed in trichloroethylene than in acetone. Besides, 0.011 wt.% of trichloroethylene still remained even after 5 hour evacuation. The value was calculated from the  $^{38}\text{Cl}$  content produced by the reaction  $^{37}\text{Cl} (n, \gamma) ^{38}\text{Cl}$ . The amount of chlorine in the specimens which did not receive any treatments with trichloroethylene was quite negligible. This indicates that appropriate cares should be taken of in preparation of the graphite specimens for experiments, especially for chemical reactions. The specimen shown in the last column of Table 2 was evacuated to  $3-4 \times 10^{-5}$  Torr for 7.5 hours and stored in closed air for 24 hours. The evacuation treatment not only made the gas volume at STP decrease but also changed the composition of gas in the pores. It was also reported by Huber<sup>5)</sup> that at most 60% of the original gas content before the degassing was reabsorbed by the graphite which had been evacuated to a degree higher than  $10^{-5}$  Torr and stored in open air, and that only about 1/50 of the amount of reabsorbed gas in the case of open air was reabsorbed by the specimen which had been stored in closed air for 200 days.

The content of argon in three kinds of graphites is shown in Fig. 3, where one can also observe the change in the content caused by heat treatment in a vacuum. The argon content ranges from about  $3.5 \times 10^{-2}$  to  $4.2 \times 10^{-2}$  % of the specimen volume, while the level-off value at higher heat-treatment temperatures is  $1.2 \times 10^{-2}$  to  $1.5 \times 10^{-2}$  vol.%. If it is assumed that the ratio of volumes of argon to the total gas in the open pores is almost the same as that in the closed pores, the values obtained above would indicate that the volume of closed pores is about 35% of the total pore volume. It is noted that, from the comparison of the release curve below  $150^\circ\text{C}$  for 7477PT with other release curves, argon is released more easily from 7477PT than from the other two graphites. Figure 4 shows the argon content and its change caused by heat-treating the specimens evacuated and stored in air. As described previously, the treatment decreases the argon content of both graphites and the amount of decrease is more pronounced for SMI-24 than for 7477PT. The fact suggests that the release of argon, and possibly of other kinds of gases, and the 're-filling'

of gases would take place more easily for 7477PT. The arguments on the easier gas release will more clearly be made in Section 3.2.3, where the release rate is estimated directly from the results of mass-spectrometry. It is also found that the level-off values range from about  $1.3$  to  $1.5 \times 10^{-2}$  vol.%, as was the case for the ordinary specimens shown in Fig. 3. This also suggests that these level-off values correspond to the volume of closed pores. That is, the fact that these values are in good agreement with those in Fig. 3 must indicate that  $1.3$  to  $1.5 \times 10^{-2}$  vol.% of argon might be present in the gas in closed pores.

### 3.2 Gas mass-spectrometry

#### 3.2.1 Composition of released gas

Background was subtracted from the peak height corresponding to each mass number. Mass-spectrometry was carried out for standard air. The peak height and the value in vol.% of each gas constituent in air, which is shown in the literature<sup>6)</sup>, were compared with each other in order to obtain a relative sensitivity, which we call here 'compensation factor'. The gas composition was calculated by multiplying the peak height by the compensation factor for each gas. The compensation factor of water was assumed to be unity in the present work.

Table 3 shows the compensation factor for each gas in air as well as the process of calculating it. Composition of the gas released from SMI-24 graphite is shown in Table 4 as a function of duration of measurement. The specimen in a glass tube was immersed in liquid nitrogen bath for 5 min and evacuated for 1 min to a degree of  $10^{-4}$  Torr. After that, the tube was kept at room temperature for 5 min and the mass-spectrogram of the released gas was measured. The result of this measurement is shown in the column represented as 0-5 min in Table 4. Mass-spectrometry was carried out for the gas released from the specimen during next 5 min in the same manner as for initial 5 min, and so on. After specimen was evacuated for mass-spectrogram for 20 hours, the glass tube containing the specimen was heated at  $280^{\circ}\text{C}$  for 30 min with closing the tap connected to the gas inlet system. Then the tube was kept at room temperature for 24 hours and mass-spectrometry was carried out for the released gas. Figure 5 shows the chart obtained by means of mass-spectrometry for gas released during a period of 2-20 hours. Constituents of the gas released from the heated specimen are shown in Fig. 6. Varicus hydrocarbons were released by heating the specimen

at 280°C though the treatment was performed after the specimen was evacuated at room temperature for 20 hours. The fact indicates that the gas released from the heated graphite is quite different in composition from that in the case of the specimen with no heat treatment, and that the meaning of gas release experiment changes corresponding to particular experimental conditions. The specimens evacuated to  $3.4 \times 10^{-5}$  Torr for 7.5 hours and stored in closed air for 24 hours, which were specified in Section 3.1, were connected to the gas inlet system and mass-spectrometry was carried out for them on the same day when the activation analysis was performed for the specimens prepared in the same way as for mass-spectrometry. The results are shown for SMI-24 and 7477PT graphites in Tables 5 and 6, respectively.

### 3.2.2 Measurements of volume of released gas

Tables 7 and 8 show the volume of gases released from SMI-24 and 7477PT measured using an Atlas CH4 mass-spectrometer. Values in the column 'Gas total' were calculated from the pressure of total released gas in the reservoir, and the volumes shown in other columns were calculated from the peak height of each gas. Release rate was estimated by dividing the value of 'gas total' by the duration time. Argon content for SMI-24 is 0.29% of the total gas volume, which agrees well with the value obtained by use of CH7 mass-spectrometer. In the case of 7477PT, argon content is so small, i.e. a several hundredths % of the total gas volume, that one cannot use the data obtained by mass-spectrometric measurements for assessing the result of activation analysis. However, Ar found shown in Table 8 and that shown in Table 6 coincide with each other. The volume of other gases, especially H<sub>2</sub>O, O<sub>2</sub> and CO<sub>2</sub>, fairly depends on the condition for preparing specimens. It is found, however, in all the experiments that the main part of the released gas is water. This agrees well with the observations made by Huber<sup>5)</sup>. A mass-spectrometric experiment was carried out for the released gas. The air, which is present in the space between the specimen and tube wall, was believed to be displaced in advance by helium at a flow rate of 1 l/min for 3 min. The result of this experiment is shown in Table 9. Total gas volume is almost the same as that in Tables 7 and 8, but the amount of water is much smaller than that found in Tables 7 and 8, whereas the larger amount of (N<sub>2</sub>+CO) is detected, which suggests the existence of residue of air in the glass tube.

Fig. 7 shows a schematic diagram of the technique for an experiment

which was carried out in order to trap the released gas using active charcoal. First, taps C<sub>1</sub> and C<sub>2</sub> were opened and helium was let in at a rate of 1 l/min for 3 min. After tap C<sub>1</sub> was closed the system was evacuated for 5 min using an oil diffusion pump backed by an oil rotary pump. The first run was carried out after specimen tube was kept at room temperature for 10 min. The second and third runs were carried out after heating at 80°C for 10 min and 160°C for 5 min, respectively. The result is not shown in detail here, because it was very complicated and seemed to have little relations with the main line of the present discussion. However, it was found that the volume of the total released gas is one-fifth of that obtained in the other experiments and that H<sub>2</sub>O, N<sub>2</sub> and CO<sub>2</sub> were about 10%, 50% and 40% of the total gas volume, respectively. It was indicated that the technique shown in Fig. 7 was irrelevant to the measurement of the volume and composition of the gas released from the open pore of graphite, at least in the experimental conditions chosen here. The specimen of SMI-24 used for the experiment which gave the result shown in Table 7 was re-evacuated for 10 min in a vacuum of 10<sup>-5</sup> Torr. After that, argon was flowed for 5 min and the specimen was stored in argon of 1 atm for 10 days. Argon found was  $9.2 \times 10^{-4}$  ml, i.e. 0.03 vol % of the specimen volume and the total gas released was 0.22% of the specimen. No water was detected.

### 3.2.3 Rate of gas release

Comparing the release rates shown in Tables 7,8 and 9, the rate for SMI-24 is about one order smaller than that for 7477PT. This corresponds to the fact that in the curves for change in argon content shown in Fig. 3 argon release due to heat treatment occurs more easily for 7477PT graphite than for SMI-24. This would result from the fact that pore size distribution curve is fairly broad and large amount in volume of pores smaller than about 1 μm are present in the case of SMI-24, whereas for 7477PT the curve is narrow and the pores are relatively homogeneous (between 1 μm and 5 μm in diameter) and rather large. Figures 8 and 9 show the results of mercury porosimetry for SMI-24 and 7477PT, respectively, from which one can also derive the preceding point of view.

### 3.3 Calculation of porosity by means of activation analysis and mass spectrometry

As seen in Table 4 and Fig. 3, in the case of SMI-24, argon content

is about 0.3 vol % of the total gas volume, and the argon found by means of activation analysis is about  $4 \times 10^{-2}$  vol % of the specimen volume so that the total pore volume can be estimated as

$$4 \times 10^{-2} \times \frac{100}{0.3} \sim 13 \text{ (vol \% of the specimen volume).}$$

Here it is assumed that the argon contents in vol % are the same both in open pores and closed pores. As the true and apparent density of SM1-24 were measured as 2.22<sup>7)</sup> and 1.76 g/cm<sup>3</sup>, respectively, the total pore volume is believed to be about 20% of the specimen volume. There are some reasons to be considered why the difference between these values is so large. Firstly, there is a possibility that the assumption made above might not be applicable to the present calculation, i.e. the gas composition is different between in open pores and closed pores. Secondly, there is another possibility that the gas in very large open pores is evacuated at the earlier stage of the experiment and cannot be detected by the mass-spectrometer. This is suggested by the result of mercury porosimetry shown in Fig. 8. The pore with the diameter larger than 10  $\mu\text{m}$  (at pressure less than about 1 atm) may be believed to be evacuated very easily. This figure indicates that the volume of pores larger than about 10  $\mu\text{m}$  is 3 to 4% of the specimen. By adding this value to that estimated from the results of activation analysis and mass-spectrometry it becomes possible to deduce the pore volume of SM1-24 graphite as about 17%, which can be considered to correspond to the level designated as E in Fig. 8. The difference between the total porosity, i.e. 20%, and the value above, i.e. 17%, would originate in the possibility that the smaller pores, voids, cracks, crystalline distortions etc. in the atomic scale cannot be detected by any of the three techniques, i.e. mercury porosimetry, activation analysis and gas mass-spectrometry, employed here. The last method would be excluded in principle, if we assume that the smaller pores are closed. In Fig. 8 the steep increase in the penetration volume, which is found in the pore diameter range of less than about  $3 \times 10^{-2}$   $\mu\text{m}$  would correspond to the fact that the mercury porosimetry can cause damage to graphite at higher pressures, as was reported in the literatures<sup>8,9)</sup>.

These arguments enable us to visualize the structure of pores in graphite as follows. Firstly, about 3% of the specimen volume is occupied by very small pores and cracks which are present between the basal planes or more generally by some kinds of lattice distortions and other deviations from the perfect crystal in the atomic scale. The porosity caused by these

smaller pores and cracks cannot be detected by either of the three techniques above. Secondly, about 6% of the volume is occupied by what is called closed pores. These pores would correspond to the level off values in Figs. 3 and 4, and the curve DE in Fig. 8. Thirdly, about 11% of the volume is the porosity which results from the larger pores, which would correspond to the difference between the initial value and the level off values in Fig. 3, and to the curve ABCD in Fig. 8. Thus we conclude that about 15% of the porosity results from the very small pores and cracks in the atomic scale, about 30% of it from what is called closed pores and about 55% of it from the open pores.

The argument above seems to us reasonable, though it is fairly difficult to apply the similar consideration to 7477PT graphite because of the smaller amount of argon in the graphite. However, from the result of mercury porosimetry shown in Fig. 9, we can deduce that the curve DE would correspond to the 'closed pores', i.e. about 5% of the specimen volume is occupied by the closed pores which, in this context, imply both the crystalline defects and lattice distortions in the atomic scale, and the microfissures accessible by mercury porosimetry at higher pressures. Remaining 14 or 15% of the volume would result from the open pores. The estimation on the open and closed pores here is believed to agree well with the idea and data of Turkdogan et al<sup>10</sup>).

#### 4. Conclusions

Conclusions derived from the present experiments are as follows.

- (1) It is estimated from the results of activation analysis, gas mass-spectrometry and mercury porosimetry for SMI-24 graphite that the open and closed pores occupy about 17% of the specimen volume. About 3% of the specimen volume is considered to originate in the crystalline distortions and defects of the atomic scale which cannot be detected by either of activation analysis, mass-spectrometry or mercury porosimetry. An argument similar to that above can be made in the case of 7477PT graphite.
- (2) Activation analysis shows that washing of specimens in a solvent such as acetone or trichloroethylene not only decreases the argon content but also changes the composition of gas in graphite, which is also influenced by 'evacuating and re-filling treatments'.
- (3) The release rate of the constituents of gas in the open pores is about one order larger for 7477PT than for SMI-24, which corresponds to the fact shown in the argon content - heat treatment temperature curves that argon

is most easily released in case of 7477PT comparing with SMI-24 and H327 graphites. These phenomena can be attributable to the difference in the pore structure between the graphites, which is discernible by means of mercury porosimetry.

(4) Change in the composition of released gas is caused by heat-treatment at lower temperature even if the specimen is evacuated for a long time before heat-treated.

(5) Though some experiments were carried out in order to determine an absolute value of volume of gas released from poly-graphite, no reasonable result was obtained at the present stage. New techniques should be conceived in future.

#### Acknowledgements

The authors wish to thank Mr. Y. Fukuda for his experimental work on mercury porosimetry. Thanks are also due to the members of the Graphite Research Laboratory, JAERI for their informative advice and discussions, and to Drs. K. Motojima and T. Komori for their interests and encouragements for this investigation.

#### References

- 1) P. Wagner, J.A. O'Rourke and P.E. Armstrong, J. Am. Cer. Soc. 55 (1972) 214.
- 2) S.K. Rhee, *ibid*, 580.
- 3) J.B.F. Champlin, Nucl. Sci. Tech. 8 (1970) 283.
- 4) B.W. Ashton, V.Y. Labaton and A. Smith, Proc. 3rd Conf. on Industrial Carbons and Graphite, Soc. Chem. Industry, London (1971) p.329.
- 5) W. Huber, Carbon 11 (1973) 655.
- 6) Rikagaku-jiten, 3rd edition, ed. by B. Tamamushi, Iwanami, Tokyo (1970).
- 7) K. Fujii, private communication.
- 8) J.M. Dickinson and J.W. Shore, Carbon 6 (1968) 937.
- 9) D.J. Baker and J.B. Morris, Carbon 9 (1971) 687.
- 10) E.T. Turkdogan, R.G. Olsson and J.V. Vinters, Carbon 8 (1970) 545.

Table 1 List of the graphites used in the experiments

| Brand   | Coke                   | Method of production | Density (g/cm <sup>3</sup> ) | Young's modulus (10 <sup>3</sup> kg/mm <sup>2</sup> ) | Manufacturer            |
|---------|------------------------|----------------------|------------------------------|---|-------------------------|
| SM1-24  | Petroleum              | Mould                | 1.76                         | 0.90  | Anglo Great Lakes Corp. |
| 7477/PT | Petroleum fine-grained | Mould                | 1.74                         | 0.98  | Le Carbone Lorraine     |
| H327    | Petroleum needle       | Extrusion            | 1.78                         | 1.51  | Great Lakes Corp.       |

The values are for the specimens parallel to the axis of press or extrusion.

Table 2 Effect of pre-irradiation treatment on the content of argon in SM1-24 graphite

| Treatment<br>Specimen | No treatment | Washed by acetone | Washed by trichloroethylene | Retained in air after vacuumized |
|-----------------------|--------------|-------------------|-----------------------------|----------------------------------|
| 1                     | 4.03         | 3.63              | 2.70                        | 2.20                             |
| 2                     | 3.64         | 3.33              | 2.49                        | -                                |
| 3                     | 4.23         | -                 | -                           | -                                |
| 4                     | 4.20         | -                 | -                           | -                                |



Table 2 Compensation factors for gases in air

| Gas<br>(Mass<br>number)   | Vol. %<br>in<br>Air<br>(V) | Peak height<br>(gas mass-<br>spectrometry)<br>(g) | Peak height<br>percent<br>(G) | Compensation<br>factor<br>(V/G)          |
|---------------------------|----------------------------|---|-------------------------------|--|
| Nitrogen<br>(28)          | 78.10                      | 173.7<br>166.3<br>170.4                           | 80.63<br>80.52<br>80.52       | 0.9686<br>0.9699<br>av. 0.9699<br>0.9694 |
| Oxygen<br>(32)            | 20.93                      | 37.8<br>36.0<br>37.3                              | 17.55<br>17.43<br>17.62       | 1.193<br>1.201<br>av. 1.188<br>1.194     |
| Argon<br>(40)             | 0.9325                     | 3.40<br>3.48<br>3.35                              | 1.57<br>1.68<br>1.58          | 0.594<br>0.555<br>av. 0.591<br>0.580     |
| Carbon<br>dioxide<br>(44) | 0.03                       | 0.454<br>0.469<br>0.462                           | 0.211<br>0.227<br>0.218       | 0.142<br>0.132<br>av. 0.138<br>0.137     |
| Water<br>(18)             | -                          | 0.06<br>0.26<br>0.10                              | 0.027<br>0.125<br>0.047       | (1.000)                                  |

Table 4 Composition of the gas released from SM1-24 graphite

| Mass number | Gas               | Duration    |       |             |       |             |       |             |       |             |       | Peak height total | Vol % |
|-------------|-------------------|-------------|-------|-------------|-------|-------------|-------|-------------|-------|-------------|-------|-------------------|-------|
|             |                   | 0-5 min     |       | 5-10 min    |       | 10-60 min   |       | 1-2 hr      |       | 2-20 hr     |       |                   |       |
|             |                   | Peak height | Vol % | Peak height | Vol % | Peak height | Vol % | Peak height | Vol % | Peak height | Vol % |                   |       |
| 18          | H <sub>2</sub> O  | 0.70        | 7.02  | 64.8        | 88.0  | 47.5        | 87.6  | 46.2        | 84.6  | 21.2        | 76.9  | 180.4             | 82.0  |
| 28          | CO+N <sub>2</sub> | 6.38        | 62.0  | 5.78        | 7.60  | 4.58        | 8.19  | 5.97        | 10.6  | 4.89        | 17.2  | 27.60             | 12.2  |
| 32          | O <sub>2</sub>    | 2.08        | 24.9  | 1.72        | 2.78  | 1.26        | 2.77  | 1.50        | 3.27  | 0.985       | 4.28  | 7.55              | 4.09  |
| 40          | Ar                | 0.264       | 1.53  | 0.264       | 0.208 | 0.219       | 0.404 | 0.249       | 0.263 | 0.199       | 0.417 | 1.20              | 0.316 |
| 44          | CO <sub>2</sub>   | 3.36        | 4.61  | 7.68        | 1.43  | 4.88        | 1.23  | 5.23        | 1.31  | 2.50        | 1.25  | 23.65             | 1.47  |

Table 5 Gas composition of the pre-evacuated specimen of SMI-24 graphite

| Mass number | Gas               | Duration (hr) |       |             |       | Peak height total | Vol % |
|-------------|-------------------|---------------|-------|-------------|-------|-------------------|-------|
|             |                   | 0~22          |       | 22~47.5     |       |                   |       |
|             |                   | Peak height   | Vol % | Peak height | Vol % |                   |       |
| 18          | H <sub>2</sub> O  | -             |       | 65.3        | 89.7  | 65.3              | 72.6  |
| 28          | CO+N <sub>2</sub> | 10.3          | 58.1  | 5.70        | 7.60  | 16.0              | 17.2  |
| 32          | O <sub>2</sub>    | 2.70          | 18.7  | 1.17        | 1.92  | 3.87              | 5.07  |
| 40          | Ar                | 0.24          | 0.81  | 0.11        | 0.089 | 0.35              | 0.226 |
| 44          | CO <sub>2</sub>   | 28.0          | 22.4  | 3.77        | 0.722 | 31.8              | 4.85  |

Table 6 Composition of the gas released from the pre-evacuated specimen of 7477PT graphite

| Mass number   | Gas | Duration (hr)     |        |             |         | Peak height total | Vol % |      |
|---------------|-----|-------------------|--------|-------------|---------|-------------------|-------|------|
|               |     | 0~24              |        | 24~43       |         |                   |       |      |
|               |     | Peak height       | Vol %  | Peak height | Vol %   |                   |       |      |
| Specimen No.2 | 18  | H <sub>2</sub> O  | 13     | 58.5        | 58.7    | 96.2              | 71.7  | 86.2 |
|               | 28  | CO+N <sub>2</sub> | 6.83   | 29.8        | 1.41    | 2.25              | 8.24  | 9.60 |
|               | 32  | O <sub>2</sub>    | 2.14   | 11.5        | 0.50    | 0.989             | 2.64  | 3.79 |
|               | 40  | Ar                | 0.070  | 0.19        | 0.010   | 0.01              | 0.080 | 0.06 |
|               | 44  | CO <sub>2</sub>   | -      |             | 2.28    | 0.51              | 2.28  | 0.38 |
| Specimen No.1 |     |                   | 0 ~ 25 |             | 25 ~ 44 |                   |       |      |
|               | 18  | H <sub>2</sub> O  | 6      | 54.2        | 75.0    | 93.4              | 81.0  | 88.6 |
|               | 28  | CO+N <sub>2</sub> | 2.48   | 21.7        | 4.57    | 5.52              | 7.05  | 7.49 |
|               | 32  | O <sub>2</sub>    | 2.19   | 23.6        | 0.325   | 0.48              | 2.52  | 3.29 |
|               | 40  | Ar                | 0.096  | 0.51        | 0.016   | 0.01              | 0.112 | 0.07 |
|               | 44  | CO <sub>2</sub>   | -      |             | 3.76    | 0.64              | 3.76  | 0.56 |

Table 7 Volume of gases released from SM1-24 graphite by means of an Atlas CH4 mass-spectrometer

| Duration<br>(min) | Gas (ml)             |                      |                |                      |                      | Gas<br>total*<br>(ml) | Release<br>rate<br>(ml/min) |
|-------------------|----------------------|----------------------|----------------|----------------------|----------------------|-----------------------|-----------------------------|
|                   | H <sub>2</sub> O     | N <sub>2</sub> +CO   | O <sub>2</sub> | Ar                   | CO <sub>2</sub>      |                       |                             |
| 0-5               | 1.5×10 <sup>-4</sup> | 1.3×10 <sup>-3</sup> | -              | -                    | 3.9×10 <sup>-3</sup> | 5.35×10 <sup>-3</sup> | 1.07×10 <sup>-3</sup>       |
| 5-22              | 4.9×10 <sup>-2</sup> | 3.7×10 <sup>-3</sup> | -              | 8.6×10 <sup>-5</sup> | 5.1×10 <sup>-3</sup> | 4.2 ×10 <sup>-2</sup> | 2.4 ×10 <sup>-3</sup>       |
| 22-57             | 1.3×10 <sup>-2</sup> | 3.0×10 <sup>-4</sup> | -              | 4.7×10 <sup>-5</sup> | 2.9×10 <sup>-3</sup> | 1.3 ×10 <sup>-2</sup> | 3.7 ×10 <sup>-4</sup>       |
| 57-127            | 3.3×10 <sup>-4</sup> | 2.2×10 <sup>-4</sup> | -              | -                    | 1.8×10 <sup>-3</sup> | 2.3 ×10 <sup>-3</sup> | 3.3 ×10 <sup>-5</sup>       |
| 127-206           | 8.5×10 <sup>-5</sup> | 1.0×10 <sup>-4</sup> | -              | -                    | 1.2×10 <sup>-3</sup> | 2.5 ×10 <sup>-3</sup> | 2.8 ×10 <sup>-5</sup>       |
| 206-527           | -                    | 1.1×10 <sup>-4</sup> | -              | -                    | -                    | 1.9 ×10 <sup>-3</sup> | 5.9 ×10 <sup>-6</sup>       |
| 527-1307          | 1.0×10 <sup>-3</sup> | 9.9×10 <sup>-4</sup> | -              | 5.2×10 <sup>-5</sup> | 7.3×10 <sup>-4</sup> | 2.9 ×10 <sup>-3</sup> | 3.7 ×10 <sup>-6</sup>       |
| Σ                 | 5.0×10 <sup>-2</sup> | 6.7×10 <sup>-3</sup> | -              | 1.9×10 <sup>-4</sup> | 1.6×10 <sup>-2</sup> | 6.46×10 <sup>-2</sup> |                             |

\* Values calculated from the pressure of gases in the reservoir.

\*\* Specimen : SM1-24, 2.99 ml.

Table 8 Volume of gases released from 7477 PT graphite by means of an Atlas CH4 mass-spectrometer

| Duration<br>(min) | Gas (ml)              |                       |                      |                       |                       | Gas*<br>total<br>(ml) | Release<br>rate<br>(ml/min) |
|-------------------|-----------------------|-----------------------|----------------------|-----------------------|-----------------------|-----------------------|-----------------------------|
|                   | H <sub>2</sub> O      | N <sub>2</sub> +CO    | O <sub>2</sub>       | Ar                    | CO <sub>2</sub>       |                       |                             |
| 0-5               | 6.9 ×10 <sup>-2</sup> | 1.8 ×10 <sup>-3</sup> | -                    | -                     | 7.7 ×10 <sup>-3</sup> | 1.0×10 <sup>-1</sup>  | 2.0×10 <sup>-2</sup>        |
| 5-35              | 2.8 ×10 <sup>-1</sup> | 1.5 ×10 <sup>-3</sup> | -                    | 1.7 ×10 <sup>-4</sup> | 5.7 ×10 <sup>-4</sup> | 2.8×10 <sup>-1</sup>  | 9.3×10 <sup>-2</sup>        |
| 35-200            | 3.5 ×10 <sup>-3</sup> | 9.8 ×10 <sup>-4</sup> | 3.2×10 <sup>-5</sup> | 5.0 ×10 <sup>-5</sup> | 1.3 ×10 <sup>-4</sup> | 4.7×10 <sup>-3</sup>  | 2.8×10 <sup>-5</sup>        |
| 200-1434          | -                     | 5.9 ×10 <sup>-4</sup> | -                    | -                     | -                     | 5.9×10 <sup>-4</sup>  | 4.8×10 <sup>-7</sup>        |
| Σ                 | 3.53×10 <sup>-1</sup> | 4.87×10 <sup>-1</sup> | 3.2×10 <sup>-5</sup> | 1.75×10 <sup>-4</sup> | 8.40×10 <sup>-3</sup> | 3.8×10 <sup>-1</sup>  |                             |

\* Values calculated from the pressure of gases in the reservoir.

\*\* Specimen : 7477 PT 4.75 ml.

Table 9 Gases released from a specimen of SMI-24 graphite after air in the specimen tube was displaced by helium with a flow rate of 1 l/min for 3 minutes

| Duration<br>(min) | Gas (ml)              |                       |                |                       |                       | Gas*<br>total<br>(ml) | Release<br>rate<br>(ml/min) |
|-------------------|-----------------------|-----------------------|----------------|-----------------------|-----------------------|-----------------------|-----------------------------|
|                   | H <sub>2</sub> O      | N <sub>2</sub> +CO    | O <sub>2</sub> | Ar                    | CO <sub>2</sub>       |                       |                             |
| 0-5               | $1.6 \times 10^{-4}$  | $5.8 \times 10^{-3}$  | -              | $2.4 \times 10^{-4}$  | $1.7 \times 10^{-4}$  | -                     | $9.3 \times 10^{-4}$        |
| 5-22              | $8.2 \times 10^{-3}$  | $7.3 \times 10^{-3}$  | -              | $2.3 \times 10^{-4}$  | $1.8 \times 10^{-3}$  | $1.6 \times 10^{-2}$  | $2.5 \times 10^{-4}$        |
| 22-57             | $5.6 \times 10^{-3}$  | $5.9 \times 10^{-3}$  | -              | $1.2 \times 10^{-4}$  | $1.3 \times 10^{-3}$  | $8.9 \times 10^{-3}$  | $9.8 \times 10^{-5}$        |
| 57-127            | $2.1 \times 10^{-3}$  | $4.4 \times 10^{-3}$  | -              | $9.5 \times 10^{-5}$  | $1.2 \times 10^{-4}$  | $6.9 \times 10^{-3}$  | $9.6 \times 10^{-5}$        |
| 127-206           | $9.1 \times 10^{-4}$  | $5.1 \times 10^{-3}$  | -              | $8.6 \times 10^{-5}$  | $1.0 \times 10^{-3}$  | $8.5 \times 10^{-3}$  | $1.0 \times 10^{-5}$        |
| 206-527           | $3.2 \times 10^{-4}$  | $1.5 \times 10^{-3}$  | -              | -                     | -                     | $3.2 \times 10^{-3}$  | $3.5 \times 10^{-6}$        |
| 527-1307          | $6.7 \times 10^{-4}$  | $1.3 \times 10^{-4}$  | -              | -                     | $5.3 \times 10^{-3}$  | $2.7 \times 10^{-3}$  |                             |
| Σ                 | $2.44 \times 10^{-2}$ | $3.01 \times 10^{-2}$ | -              | $7.71 \times 10^{-4}$ | $4.92 \times 10^{-3}$ | $7.05 \times 10^{-2}$ |                             |

\* Values calculated from the pressure of gas in the reservoir.

\*\* Specimen SMI-24, 2.94 ml.

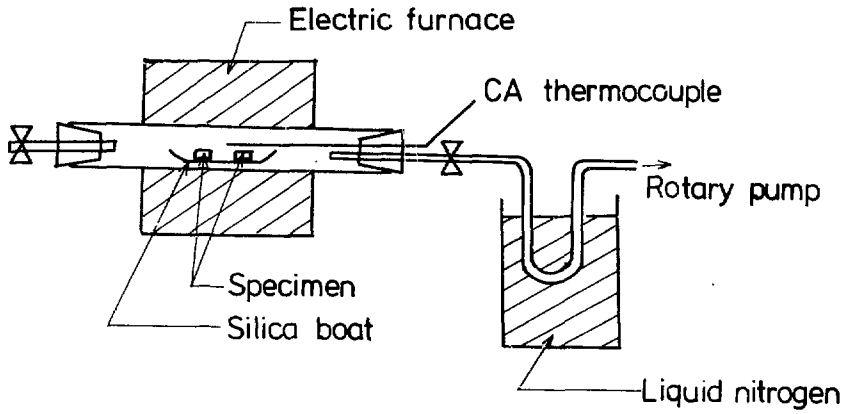


Fig. 1 Schematic diagram of the apparatus for activation analysis experiments.

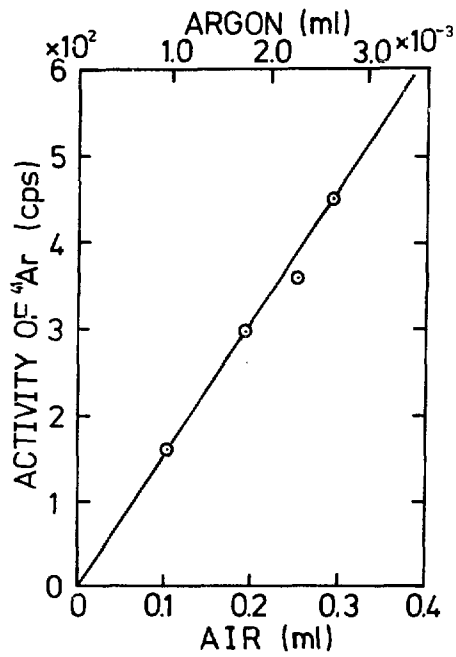


Fig. 2 An example of the calibration curve for Ar determination.

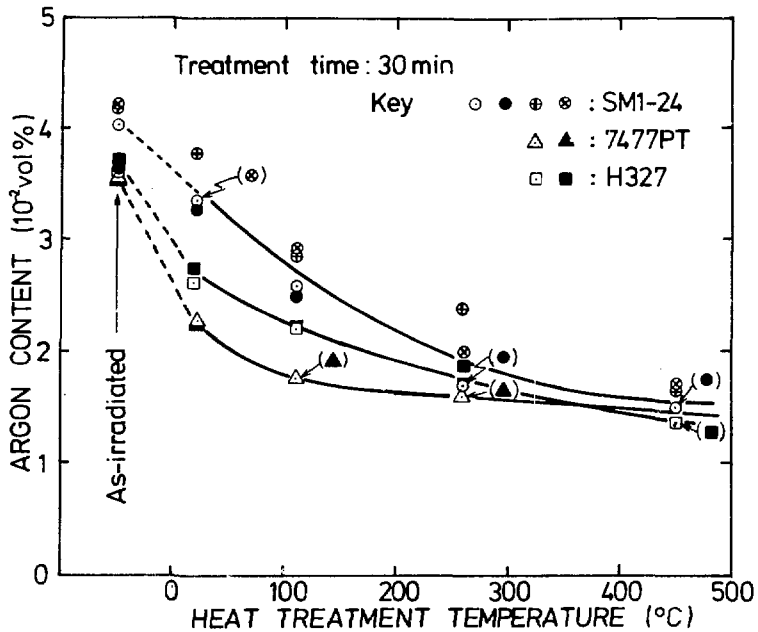


Fig. 3 Content of Ar in three kinds of graphites as a function of heat-treatment temperature.

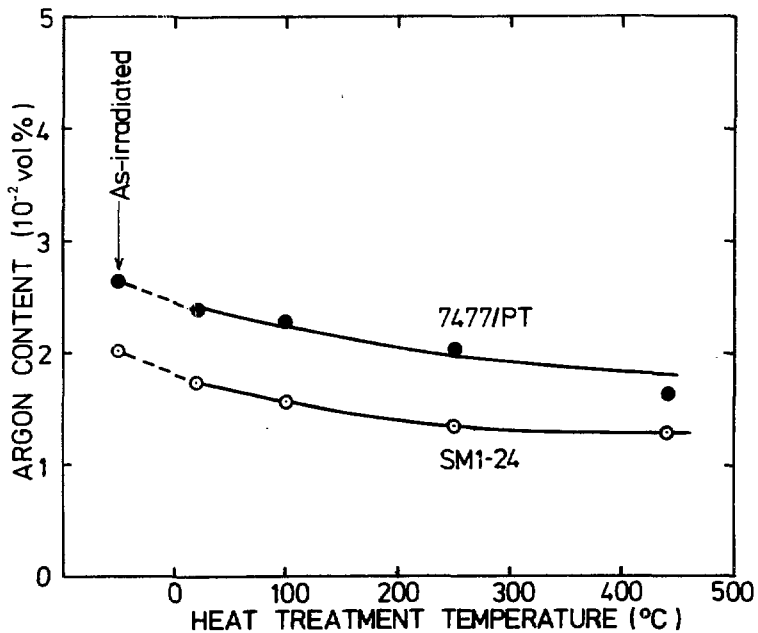


Fig. 4 Argon content and its change due to heat treatment for the specimens stored in air after evacuated.

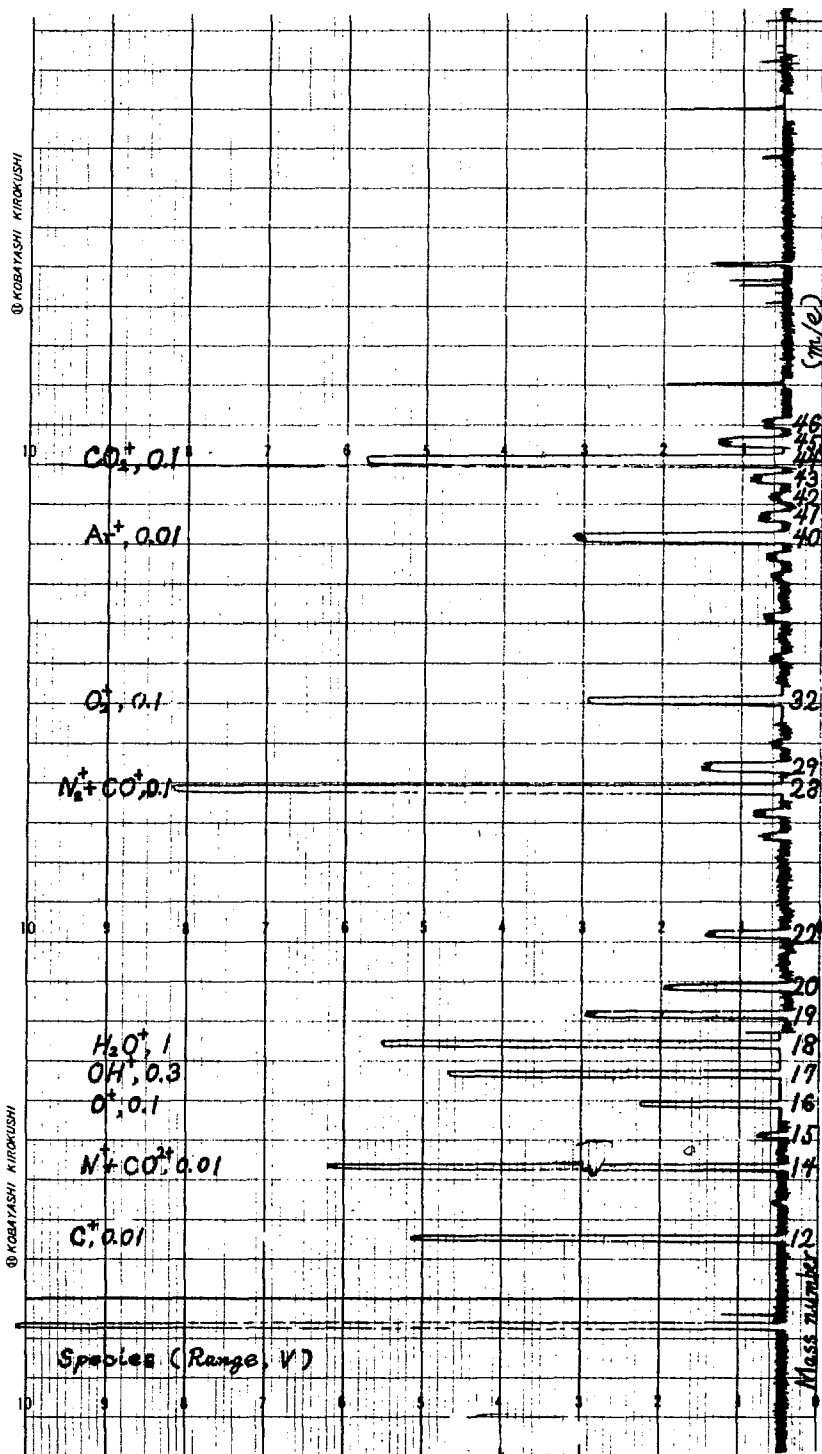


Fig. 5 Mass-spectrogram of the gas released from SMI-24 graphite during a period 2-20 hours.



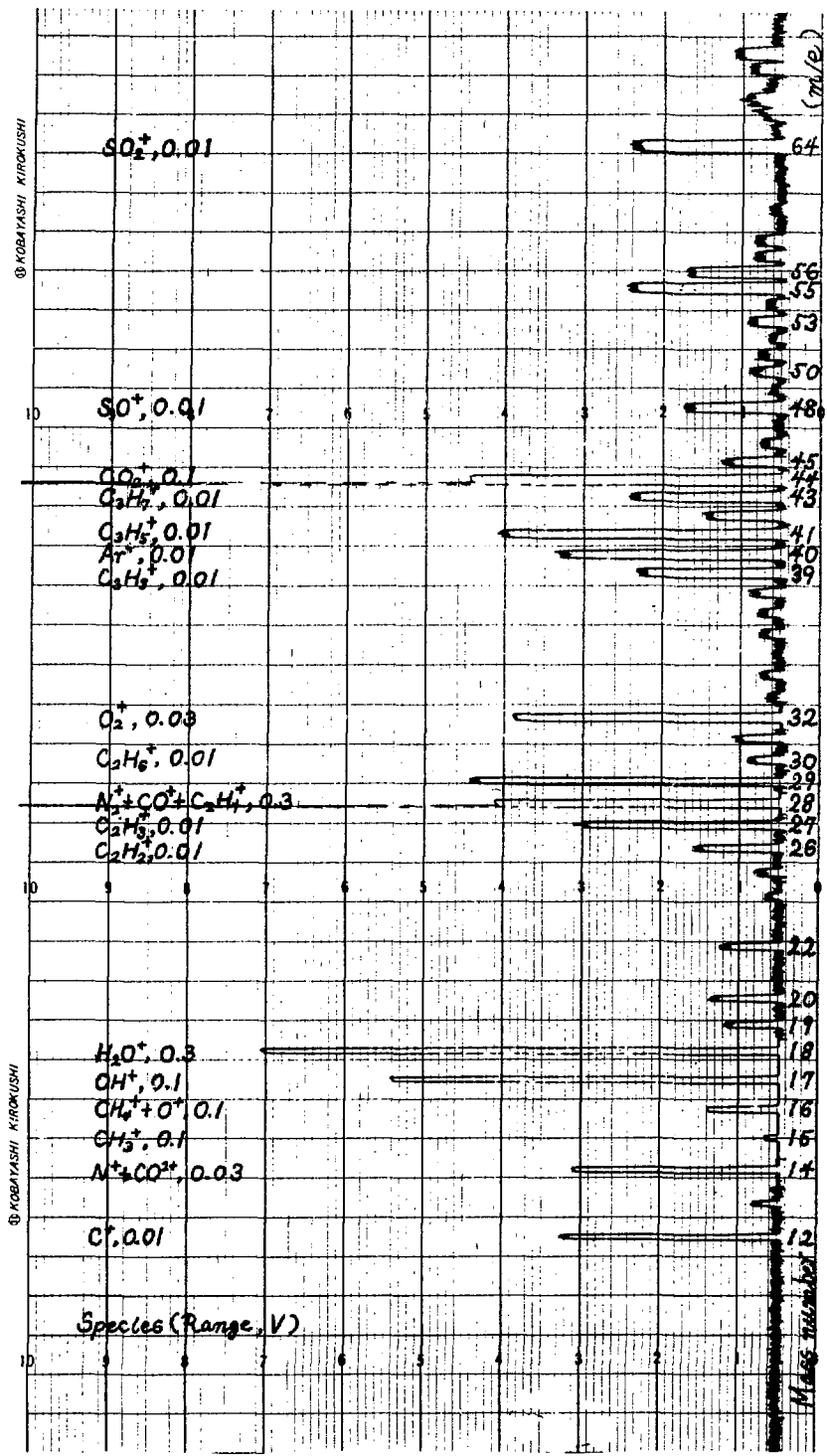


Fig. 6 Mass-spectrogram of the gas released from a SMI-24 specimen which was heated at 280°C for 30 min.

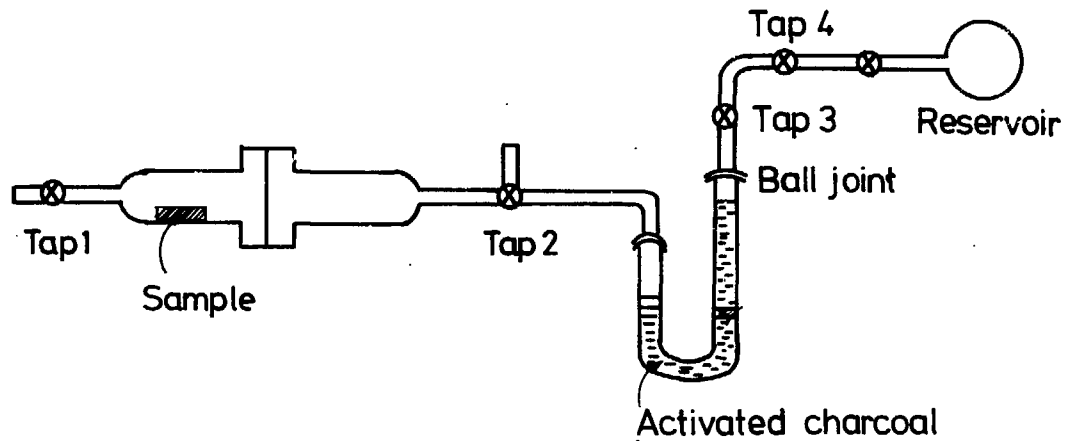


Fig. 7 Schematic diagram of the technique for an experiment carried out in order to trap the released gas with active charcoal.

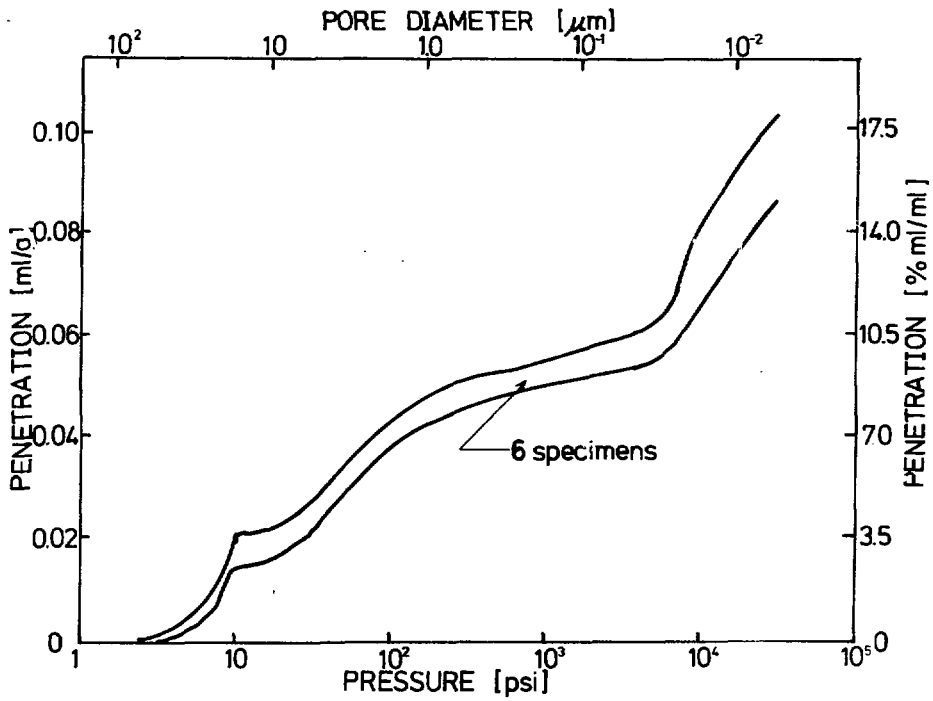


Fig. 8 Mercury porosimetry of SMI-24 graphite.

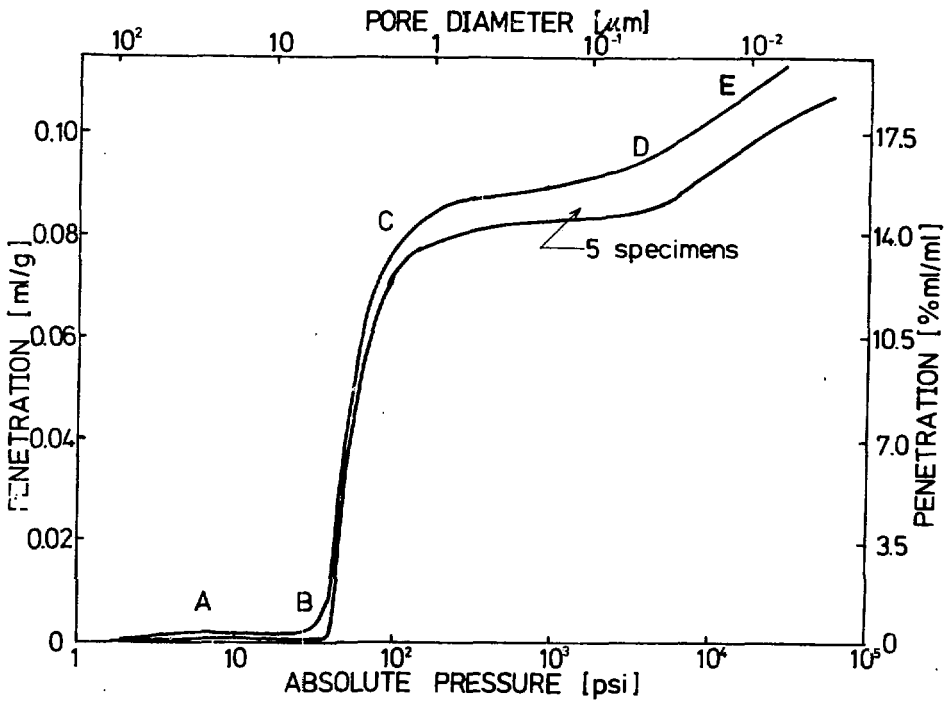


Fig. 9 Mercury porosimetry of 7477PT graphite.