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ON THE MEASUREMENT OF SPECIFIC
ENERGY OF COALS BY MEANS
OF ^{12}C DETERMINATION USING
A CORRELATION METHOD

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O POMIARZE CIEPŁA SPALANIA WĘGLA PRZY POMOCY
OKREŚLANIA ZAWARTOŚCI ^{12}C STOSUJĄC METODĘ
KORRELACYJNĄ

ОБ ИЗМЕРЕНИИ ТЕПЛОТВОРНОЙ СПОСОБНОСТИ УГЛЕЙ
ПРИ ПОМОЩИ ОПРЕДЕЛЕНИЯ СОДЕРЖАНИЯ ^{12}C
ИСПОЛЬЗУЯ КОРРЕЛЯЦИОННЫЙ МЕТОД

by

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Abstract

—The most important industrial property of coal is its gross specific energy /combustion heat/. It depends mainly on carbon concentration in coal. We propose to measure the carbon or more precisely, its ^{12}C content using the $/n,n'\gamma$ reaction in which 4.43 MeV gamma rays are emitted. We are using the correlation technique which can be used in high background measurements. The idea of correlation type measurement necessitates the existence of a reaction chain with primary and secondary radiations emitted and registered. By measuring the correlation or covariance function Φ we can obtain a measure of the number of excited ^{12}C nuclei i.e. a value which is connected to the carbon concentration.

Our experimental setup consisted of an aluminium cylinder 50 cm in diameter the height of which was also 50 cm. A central aluminium tube was put on the axis of the cylinder. Inside this tube two scintillation detectors divided by a thick lead shield were measuring primary and secondary radiations. The Pu-Be source was put on the top of the lead shield.

Six samples of ground coal-ash mixtures were measured. For each sample the measurement was repeated five times in order to get the experimental estimate of the standard deviation for each sample. This error estimate does not include the sampling error. The dependence of Φ/t ratio /t being the sampling interval time/ on carbon concentration shows a clear increase of the Φ/t value with carbon content. The relative standard deviations for different points vary from 1.3 to 4.4 %.

The preliminary results presented show that with improved experimental techniques this method can find application in industrial coal combustion heat measurements.

Резюме

Самой важной характеристикой угля при его промышленном использовании есть его теплотворная способность. Зависит она главным образом от содержания углерода. Мы предлагаем измерять концентрацию углерода / точнее ^{12}C / в промышленном угле используя ядерную реакцию $^{12}\text{C}(n, n'\gamma)^{12}\text{C}$ в которой испускаются гамма кванты с энергией 4.43 Мэв. Применяем корреляционную технику, которая обладает преимуществом малой чувствительности к фону. Суть корреляционного метода опирается на наличие цепи двух ядерных реакции, в которых так первичное как и дочерное ядра излучают гамма или бета-кванты. Получаемая величина функции корреляции Φ дает нам меру числа возбужденных ядер ^{12}C т.е. величину связанную с концентрацией углерода.

Наша измерительная установка состояла из алюминиевого цилиндра диаметром 50 см и такой же высоты. Вдоль оси цилиндра расположена внутренняя алюминиевая труба. Внутри этой трубы находятся два сцинтиляционные детектора, которых разделял толстый свинцовый экран. Один из детекторов измерял γ -кванты сопровождающие испускание нейтрона из $\text{Pu}-\text{Be}$ источника, а второй детектор регистрировал вторичное излучение из реакции неупруго рассеяния нейтронов на ^{12}C . $\text{Pu}-\text{Be}$ источник помещался на верху свинцового экрана.

Измерялись пробы взятые из шести порошковых смесей угля с золой. Для всякой пробы измерение производилось в пять раз так чтобы получить экспериментальную оценку стандартного отклонения для проб. Такая оценка погрешности не принимает во внимание погрешности связанной с побираем пробы. Зависимость Φ/t / куда t есть интервал времени в течение которого коррелируются импульсы из обоих каналов) от концентрации угля показывает на сильный рост Φ/t с ростом концентрации углерода. Относительные ошибки в величине Φ/t для разных точек имеют величину от 1.3 до 4.4 %.

Результаты работы показывают, что после усовершенствования измерительной техники, этот метод можно использовать для измерения теплотворной способности в промышленных условиях.

Streszczenie.

Najważniejszą z własności węgla opalowego jest jego ciepło spalania. Zależy ono głównie od zawartości pierwiastka węgla. Proponujemy mierzyć koncentrację C /ściślej ^{12}C / w węglu przemysłowym wykorzystując reakcję $n, n' \gamma$, w której emitowane są kwanty γ o energii 4.44 keV. Stosujemy korelacyjną technikę pomiaru, której zaletą jest możliwość przeprowadzania pomiarów także i przy wysokim poziomie tła. Istota pomiaru korelacyjnego wymaga istnienia łańcucha 2 reakcji jądrowych, w którym emitowane i rejestrowane jest promieniowanie pierwotne. Otrzymana wartość funkcji korelacji Φ daje nam miarę liczby wzbudzonych jąder ^{12}C , tj. wartość związaną z koncentracją pierwiastka węgla.

Nasze stanowisko pomiarowe składało się z aluminiowego walca o średnicy 50 cm i wysokości 50 cm. Wzdłuż osi umieszczono wewnętrzną rurę aluminiową. Wewnątrz tej rury znajdowały się dwa detektory scyntylicyjne przedzielone grubym ekranem ołowianym; detektory te mierzyły pierwotne promieniowanie ze źródła i promieniowanie wtórne pochodzące z reakcji nieelastycznego rozpraszania neutronów na węglu ^{12}C . Źródło Pu-Be umieszczone zostało na wierzchu ekranu ołowianego.

Zmierzono próbki z sześciu mieszanin popiołu ze zmielonym węglem. Dla każdej próbki pomiar powtarzano pięć razy, tak by otrzymać eksperymentalną ocenę odchylenia standardowego dla próbki. Ta ocena niepewności pomiaru nie zawiera błędu próbkowania. Zależność Φ/t /gdzie t jest interwelem próbkowania/, od zawartości węgla wykazuje wyraźny wzrost wartości Φ/t wraz ze wzrostem zawartości węgla. Względne wartości odchylenia standardowego dla poszczególnych punktów waha się od 1.3 do 4.4 %.

Wstępne rezultaty przedstawione w pracy wskazują, że po poprawieniu techniki pomiarowej, ta metoda może znaleźć zastosowanie w pomiarach ciepła spalania w warunkach przemysłowych.

1. INTRODUCTION

Coal as well as lignite belong to the most important energy resources of to-day. The quality of coal may be characterized by:

1. Its combustion heat or gross specific energy
2. Ash content
3. Moisture content
4. Sulphur content.

For the energy producing industry the most important parameter of the coal burned is its combustion heat. It is linked mainly to the carbon content of the coal, as can be inferred from combustion heat Q formulas, e.g. from one by Dulong [1]

$$Q = 81.37C + 345 \left(H - \frac{O + N - 1}{8} \right) + 22.2S \text{ [kcal]} \quad (1)$$

Here C,H,O,N,S mean the percentage concentrations of carbon, hydrogen, oxygen, nitrogen and sulphur. Therefore, if we know the C,H,O,N,S concentrations in a particular coal we can calculate the combustion heat. In an another approach we may correlate the carbon content only with the combustion heat of the coal, neglecting all minor admixtures.

In Fig.1 is shown the experimental dependence of combustion heat on carbon content only.

The experimental data come mainly from the literature [2], [3] and some samples of lignite from Turów Coal Mine made available to us by its Board of Directors.

We can see from Fig. 1 that the dependence of combustion heat Q on carbon content C may be approximated by a straight line of the type

$$Q = mC + b \quad (2)$$

where m and b are constants. The correlation coefficient $R = 0.9966$ and is very high, whereas the standard deviation Δ_1 is relatively small, as shown in the figure, $\Delta_1 = 0,3 \text{ kcal/}$
 $/\text{kg}$. Note that the value of $m = 105.8 \text{ kcal/kg \% C}$ (0.443 MJ/

/kg % C) is significantly different from the coefficient in Eq. 1. This is probably due to the intercorrelations between carbon and the other elements in the coal.

2. DISCUSSION OF MERITS OF VARIOUS METHODS OF COMBUSTION HEAT DETERMINATION

Nuclear methods currently used for the determination of combustion heat of coals are based mainly [4], [5] on transmission or backward scattering measurements of x-rays, low energy gamma, or beta radiation. Such a type of measurement detects the difference in the average atomic number Z between carbon $Z = 6$ and the ash constituents characterized by $Z \sim 15$. These methods detect therefore the ash content of the coal and from that the combustion heat is inferred. For bituminous coal the ash content is 6 - 15%, whereas the carbon content varies between 40 and 70 %. The dependence of combustion heat Q on ash content A_{ah} is shown in Fig. 2 for almost the same set of samples as used in Fig. 1. The first impression we get from this figure is that the spread of experimental points there is much higher than in the previous figure and the correlation coefficient is much lower, amounting only to 0.25. On the other hand, different parts of the plot are populated by different types of coal and therefore no universal calibration curve can be drawn. It is known from practical applications that particular curves must be obtained for different coals and even for particular pits. This fact is due to huge differences in moisture contents. On one hand we have cannel and anthracite type of coals with quite high ash but very low moisture contents, on the other we have lignite type coals with low ash but high water content.

From previous discussion the merits of using carbon content as the indicator of the value of combustion heat are well visible.

The low energy gamma ray backscattering or transmission techniques have another disadvantage, namely that the penetration depth of these types of radiation is extremely low: from

less than 1 mm for beta backscattering to 4 - 5 mm for some gamma rays. This fact is making the fine grinding of the coal necessary and causes awkward problems with sample preparation.

These difficulties can be circumvented by using neutron sources and utilizing $(n, n' \gamma)$ inelastic scattering reaction on carbon [4], [6]. The reaction threshold on ^{12}C is ~ 4.3 MeV. The gamma ray emitted by deexcitation of ^{12}C nucleus has the energy of ~ 4.44 MeV and can be easily detected using a scintillation detector. The range of this method is far greater than that of the backscattering method, being of the order of 20 cm, so that the problems of sample preparation become less acute. The measurement precision, however, is low, amounting to 5 - 8% [4]. A look at Fig. 3, showing the energy spectrum of gamma rays as measured by us on industrial graphite, makes clear the reasons for this low precision of measurement. The peaks corresponding to the gamma rays emitted from the carbon are not prominent and the background is, using bulk samples, important.

We would like to discuss here the problem of the choice of an appropriate neutron source. In principle two types of sources are possible: (α, Be) isotopic sources, as for example ^{241}Am or ^{238}Pu -Be sources, or a 14 MeV pulsed generator source. The neutron energy spectrum from, e.g., the ^{241}Am -Be source is shown in Fig. 4a, and in Fig. 4b is shown the energy dependence of the cross-section of the $(n, n' \gamma)$ reaction on ^{12}C . A fast decline of the cross-section for $E_n > 12$ MeV is visible. The neutron energy spectrum is falling from its maximum intensity at ~ 3 MeV almost linearly, reaching the zero intensity slightly above 10 MeV.

The inelastic neutron scattering on oxygen is creating unwanted gamma-ray background. The gamma rays produced here have energies of 6.13, 6.9 and 7.1 MeV. They create, through Compton scattering, unwanted background in the 3.9 - 4.8 MeV range, where the useful signal from ^{12}C is registered. The cross-section for this reaction becomes substantial at and above the neutron energy of 7.5 MeV. The spectrum of neutrons.

from the ^{241}Am -Be source shows little intensity above 8 MeV, in contrast to the 14 MeV neutron generator. Therefore, using the isotopic neutron source we should obtain a better signal to background ratio in the ^{12}C gamma ray energy window.

3. THE CORRELATION DETECTION TECHNIQUE

In the case where the measured signal is observed on a large background, it becomes worthwhile to use a correlation type measurement, which is quite insensitive to an accidental background [6], [7]. The original proposition by Goldanski and Podhorecki [7] was to use this method for measuring the lifetimes of excited states, but it can also be adapted for measurements of the quantity of excited atoms [4], i.e., in our case of the number of excited ^{12}C nuclei.

The approach by Czubek [9] is based on the theory of stochastic processes, which is more general than the argumentation of papers [6] and [7].

In order to use a correlation measurement we need the existence of the following reaction chain. A primary radiation from a neutron source excites or activates the interesting nucleus in the material under assay. This excited nucleus - the daughter product - emits a secondary radiation which can be registered. The primary radiation signal is measured by, say, detector X and the secondary radiation by detector Y. From the X and Y signals the cross-correlation function Φ can be computed for distinct time intervals

$$\Phi = \langle xy \rangle - \langle x \rangle \langle y \rangle . \quad (3)$$

Here $\langle \rangle$ means the expected values over the sampling time interval τ . If the X and Y signals are statistically independent, i.e. no causality relationship exists, then $\Phi = 0$. If, however, a parent-daughter effect is present, then some time after the emission of the primary radiation the secondary radiation is emitted. The time interval between the primary and secondary radiation will depend on the lifetime of the

excited state or of compound nucleus. We can make correlation function measurements for different lengths of time interval (to do this we will need, some special devices). If the time interval is much smaller than the lifetime of the excited state we will have very small correlation, i.e. very rarely both the primary and secondary radiation signals will be registered during the same time interval. As the length of the interval increases, more and more frequently both primary and secondary radiation signals are registered simultaneously and therefore the result of the multiplication of xy is rising. Also the correlation function will increase.

If the time interval length is so great that all secondary pulses are registered together with its primary radiation then the value of the correlation function reaches *maximum* value. For this last case Goldanski and Podhorecki [7] calculated the asymptotic value of the correlation function Φ_{as}

$$\Phi_{as} = \epsilon_x \epsilon_y \tilde{m} \quad , \quad (4)$$

where ϵ_x and ϵ_y are overall registration probabilities of radiation X and Y, \tilde{m} is the average number of decays of the excited state during the time interval τ . Thus if we use $m = \tilde{m}/\tau$, the number of decays per unit time interval, we can write

$$\Phi/\tau = \epsilon_x \epsilon_y m \quad . \quad (5)$$

If our time interval has smaller length than the "asymptotic" one, then the value of the correlation function will depend on its length, i.e. $\Phi = \Phi(\tau)$, and will read [8], [10]

$$\Phi = \epsilon_x \epsilon_y \tilde{m} f(\lambda\tau) \quad . \quad (6)$$

Here λ is the decay constant of the excited state. In the case of an excited state

$$f(\lambda\tau) = \frac{1}{\lambda} (\lambda\tau - 1 + e^{-\lambda\tau}) \quad (7)$$

/In [8] this expression contains a misprint/.

In our investigation, however, we are dealing, with a situation when the time delay is governed by the transport time. This problem has been dealt with in [10]. We have calculated the time dependence of the incoming gamma-ray signal using the MORSE [12] code. The geometric situation corresponded to our experimental setup and the neutron energy spectrum was that of the Pu-Be isotopic neutron source. The distance from source to detector was 20 cm. The results of the calculations are shown in Fig. 5. For comparison the results of [11] Lawson-Cook calculations are also shown. There is a difference between our MORSE and the Lawson-Cook results. It is due mainly to the presence of a hole in our experimental setup /see Fig.6/ through which the probe is moving. Thus no carbon is present near the source and no gamma rays are produced during the first few nanoseconds. On the other hand, the finite size of the sample diminishes the gamma ray flux a from large distances, i.e. for great time values. Therefore a more pronounced peak around medium response time is obtained. A curve of the type

$$\frac{d\phi(t)}{dt} = \sum_{m=0}^2 W_m (t - a)^m \exp(-\lambda(t-a)) \quad (8)$$

has been fitted to the MORSE calculation results and the values $a = 2 \times 10^{-9}$ s, $W_0 = 0.14$, $W_1 = 0.85$, $W_2 = 0.008$, $\lambda = 0.51 \times 10^9 \text{ s}^{-1}$ have been obtained.

The form of the curve given by eq. (8) is suggested by the equations of multiple collision expansions [13] of neutron transport phenomena, which give for the time dependent neutron flux Ψ_n the following expression

$$\Psi_n(x, \mu, \Phi, t) = \frac{e^{-t}}{t} \frac{t^n}{n!} F_n(\mu, \Psi, \eta) \quad ,$$

where $\eta = x/t$ /in this notation dimensionless/, μ is the cosine of scattering angle, F_n is called the n-th collided flux, n is the collision number and the cross-section are taken equal 1. Therefore the results of our fit suggest the

dominance of the second collision.

It has been shown in [10] that the second collision flux reaches the limiting value more slowly than does the first collision flux or in the case of excited state decay. Namely for equivalent lifetime of 2 ns the function $f(\lambda\tau)$ reaches 99 % of its asymptotic value for sampling time interval of 700 ns. Therefore for intervals larger than 1 μ s no dependence on sampling interval length will be visible.

4. EXPERIMENTAL SETUP

Our experimental setup is shown in Fig. 6. It consisted of an aluminium cylinder of 50 cm diameter and 50 cm height. The central tube was also made of aluminium with 13 cm inner diameter and with walls 6 mm thick. Inside of this tube a scintillation probe P_x with ϕ 40x40 mm NaI(Tl) crystal was counting the 4.43 MeV gamma rays accompanying the emission of neutrons from the $^{238}\text{Pu-Be}$ source placed just below the P_x detector on the top of a 18 cm thick lead shield. Below the shield a second, spectrometric scintillation detector P_y of the size ϕ 3" x3" was counting the gamma rays from inelastic scattering of neutrons on carbon nuclei.

The samples consisted of crushed coal with particle size less than 5 mm mixed with coal ash. The samples had the same volume, 91.5 dcm, but their weights varied between 35 and 75 kg. The carbon content was known from chemical analysis. For each coal-ash mixture two samples were taken and two chemical analyses were performed. Subsequently the average value was used for the carbon content. There were 6 mixtures with carbon contents ranging from 21 to 56 % by weight. The results of the chemical analyses are summarized in Table I.

The block diagram of the electronics used is shown in Fig. 7. All modules were put into a single CAMAC crate. The single channel variable sampling interval correlator has been built [14] in our Department. The multiplier has the capacity of 4x4 bits. This fact limits the radiation intensity

measured by the X detector to the average value of $\bar{X} = 3$ counts per sampling interval, e.g. when using 10 μs sampling interval the maximum intensity will be 300000 counts per second. Larger intensities will cause overflows in the multiplier and therefore a biased /lower than true/ value of the correlation function. The sampling interval time may be chosen between 1 μs and 1 s.

The time sequence was obtained from a 10 MHz crystal clock and timer where appropriate sampling interval length could be chosen. The controller made it possible to start and stop the entire measuring process and also to display the results in the form of $R_{x_1}Y_1$, R_{x_1} , Y_1 and the number of sampling intervals N.

5. THE EXPERIMENTAL RESULTS

The yield of the Pu-Be source used was 1.02×10^6 neutrons/s. The typical measurement times were 10000 s for 1 μs interval and about 2 times longer for 5 and 10 μs intervals.

The samples were measured 5 times each in order to get experimental estimate of the standard deviation for each sample. This error estimate does not include the sampling error. We used 1,5 and 10 μs sampling interval times. The ratio Φ/τ was constant for three interval sizes used as expected from previous discussion.

The results of the measurements are summarized in Table II. Fig. 8 is shown the dependence of the Φ/τ value on the carbon concentration in a unit volume. A clear increase of Φ/τ with carbon concentration is visible. The error bars in Fig. 8 correspond to the estimates of standard deviation of the measurement population and not to the errors of the average values. These standard deviations vary from 1.3 % to 4.4 %, relative to the average value.

6. CONCLUSIONS

The carbon content has been shown to be a better specific energy indicator than the ash content. The proposition to use the correlation method in conjunction with inelastic neutron scattering on ^{12}C has been shown experimentally to be basically correct. The intrinsic error of this method are quite low /approximately 3% relative/. The technical setup so far used needs further improvement, e.g., the use of a larger source and appropriate detector, before attempting an industrial application.

Table I

The results of chemical analyses of coal + ash mixtures

Sample No	Carbon content %	Ash %	Moisture %	Volatiles all %	parts H %
1	57.08	16.87	6.18	19.87	3.16
	56.25	16.85	5.97	20.93	
2	56.15	25.22	5.03	13.6	3.91
	56.01	25.40	5.08	13.51	
3	45.33	39.45	4.31	10.91	1.65
	44.74	39.47	4.31	11.48	
4	39.71	45.91	4.11	10.27	2.12
	39.70	45.86	4.07	10.37	
5	33.68	52.28	3.71	10.33	1.26
	34.09	52.19	3.56	10.16	
6	21.01	75.93	2.66	0.40	0.25
	21.17	75.21	2.79	0.83	

Table II

The results of measurements of correlation function on coal + ash mixtures

Sample No	Carbon content kg/dm ³	Sample density kg/dm ³	Average ϱ/t value	Estimated of ϱ/t value	Sigma %
1	0.458	0.8173	3.17	0.130	4.1
2	0.431	0.769	3.01	0.093	3.1
3	0.347	0.7714	2.69	0.088	3.3
4	0.298	0.7517	1.97	0.086	4.4
5	0.255	0.7528	1.79	0.024	1.3
6	0.140	0.6675	0.70	0.029	4.1

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FIGURE CAPTIONS

- Fig. 1 The dependence of combustion heat of various coals on its carbon content.
- Fig. 2 The dependence of combustion heat of various coals on ash content.
- Fig. 3 Spectrum of γ -rays from a bulk sample of industrial graphite under irradiation by neutrons. The neutron source was a 1×10^6 Pu-Be source.
- Fig. 4 a) Cross-section of $C(n, n^{\prime}\gamma)$ reaction as function of neutron energy
b) Neutron energy spectrum from $^{241}\text{Am-Be}$ source.
- Fig. 5 Gamma-ray flux time dependence calculated for coal using Monte-Carlo methods:
a) by Lawson and Cook for infinite size sample,
b) by us using MORSE [12] code and real form of sample used.
- Fig. 6 The experimental setup
- Fig. 7 Block diagram of electronics used.
- Fig. 8 The plot of correlation function per unit time interval versus carbon concentration. The error bars correspond to standard deviation of individual measurement.

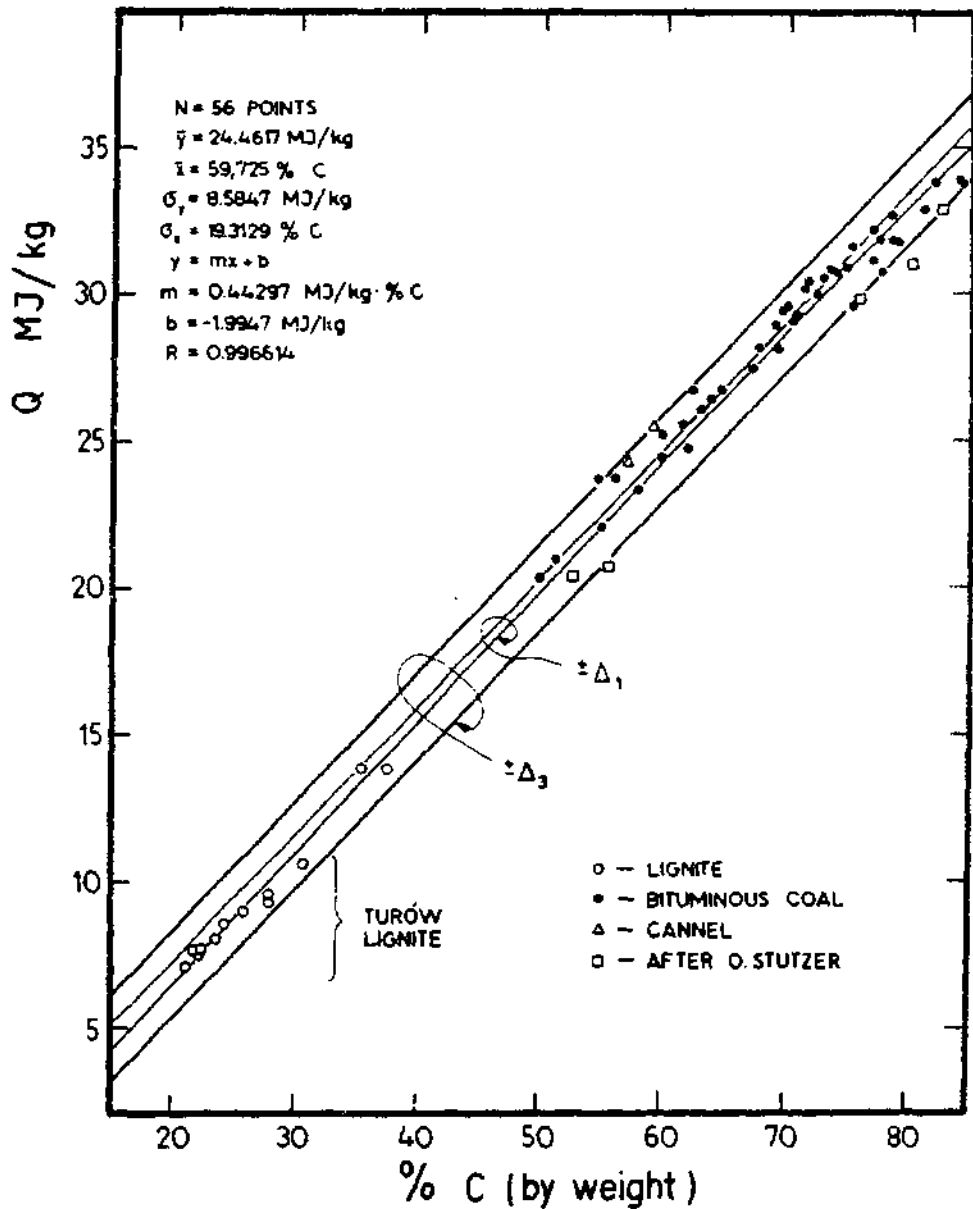
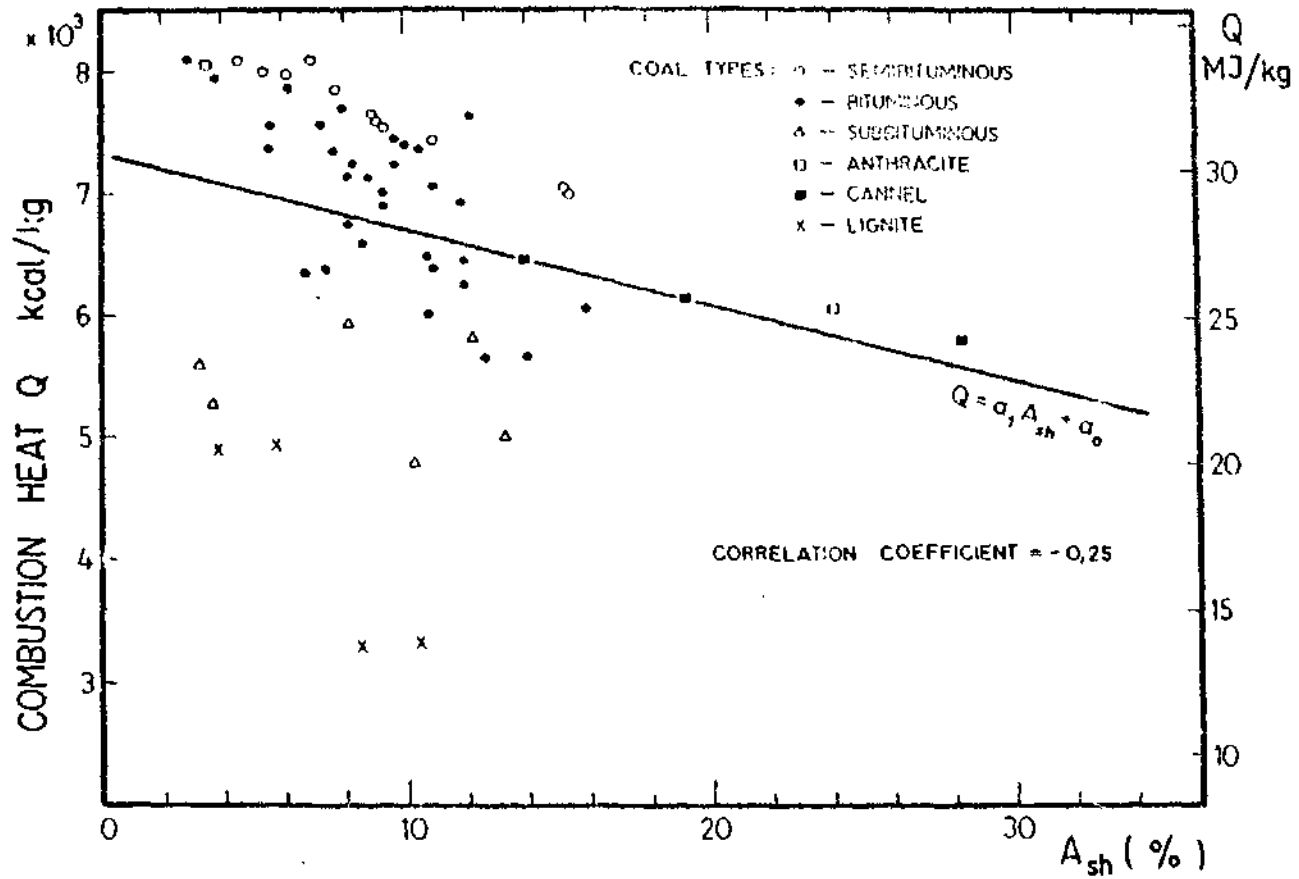


Fig. 1.



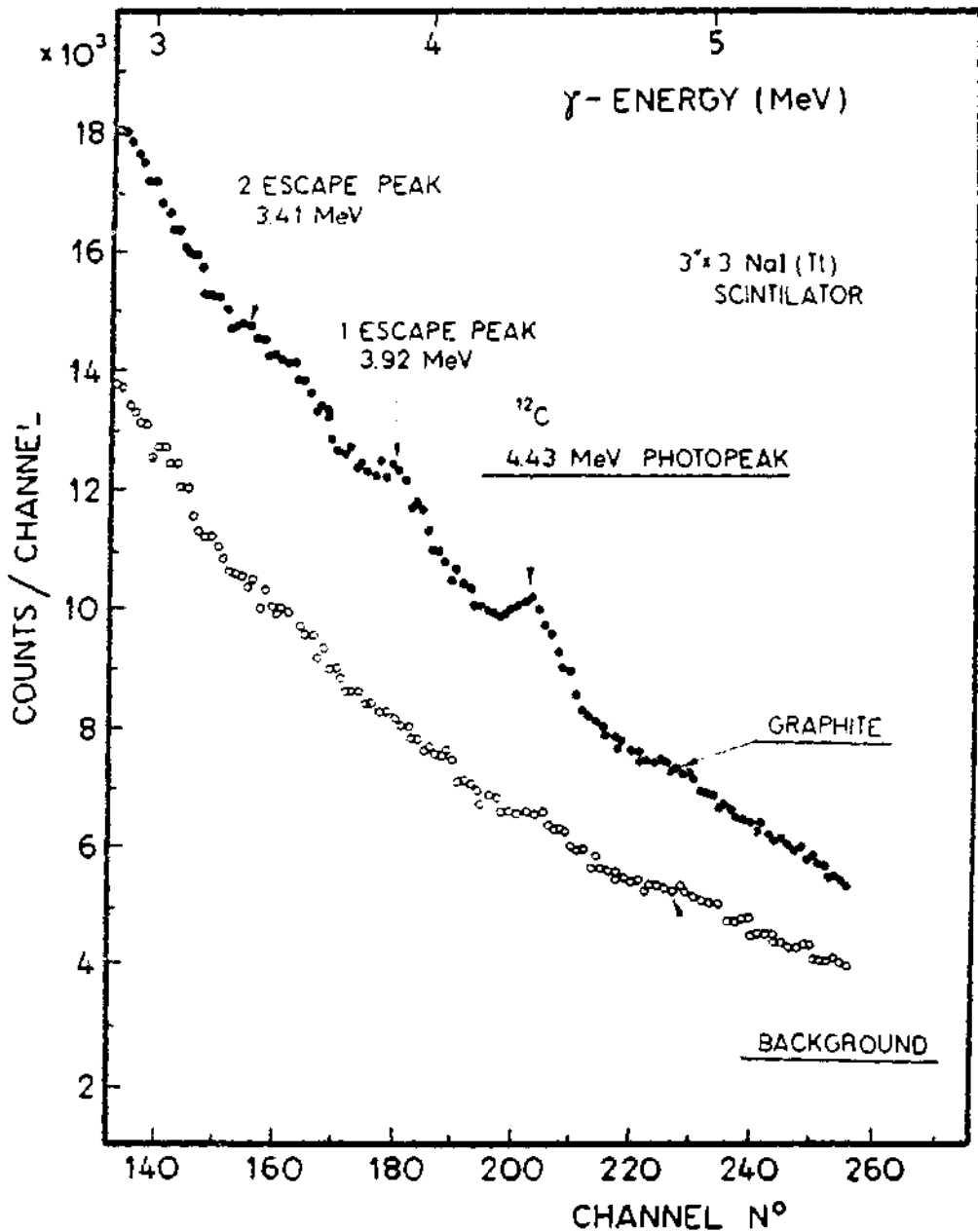


Fig. 3.

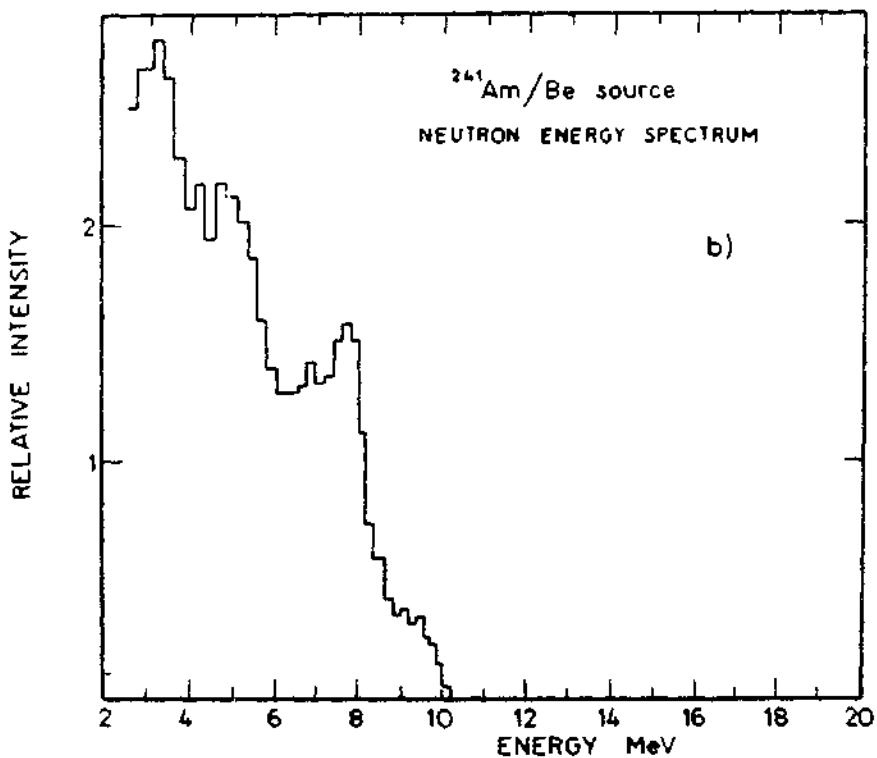
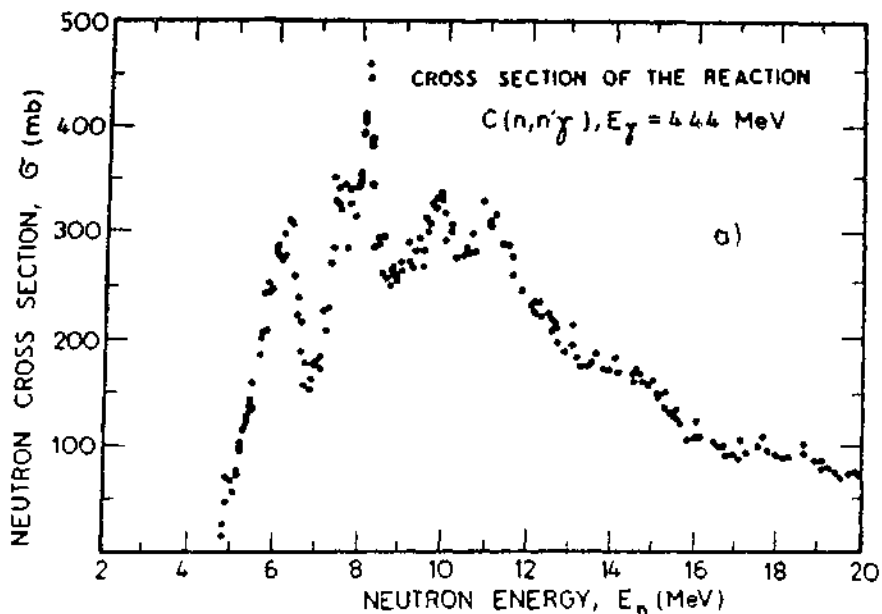


Fig.4.

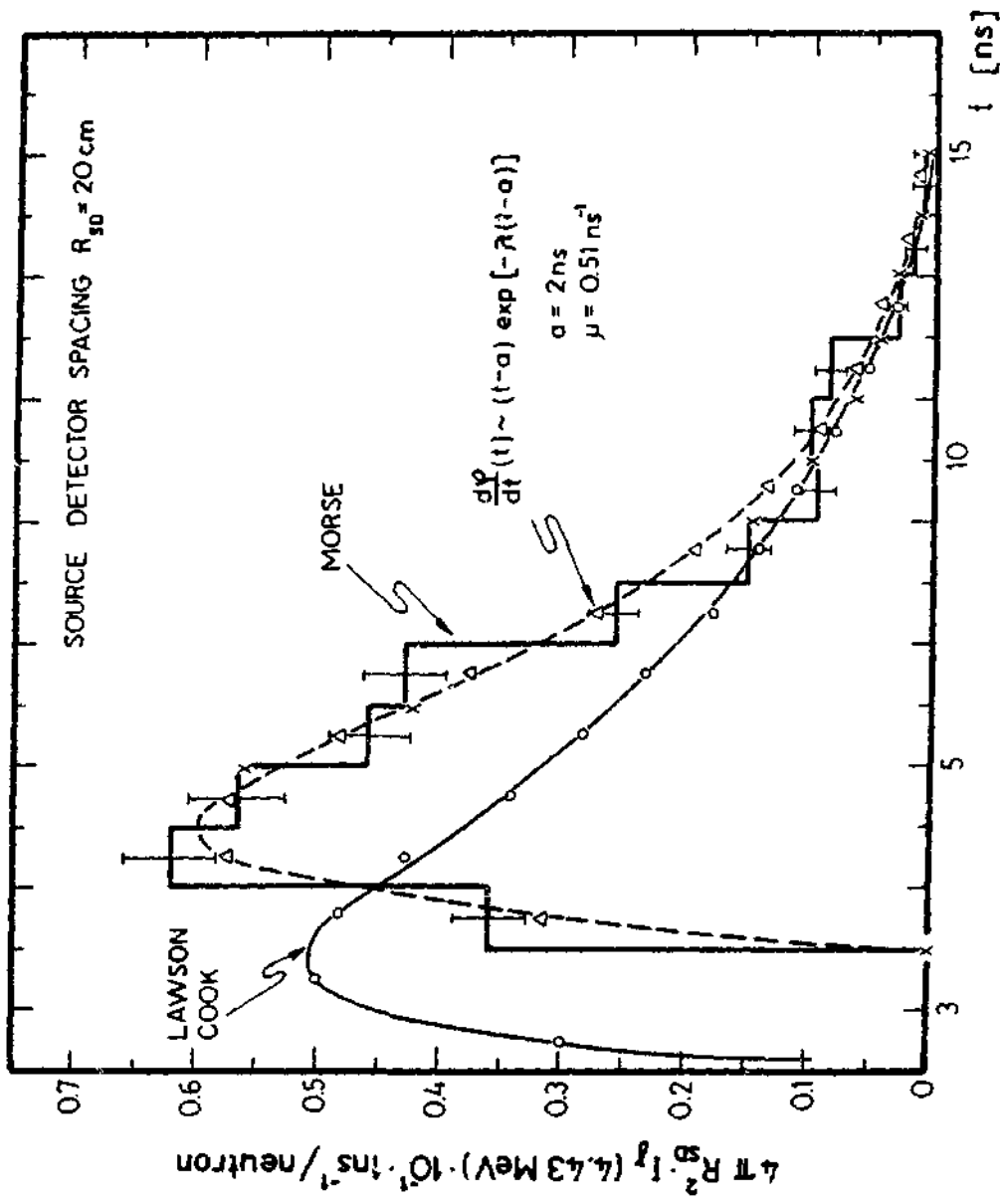


Fig. 5.

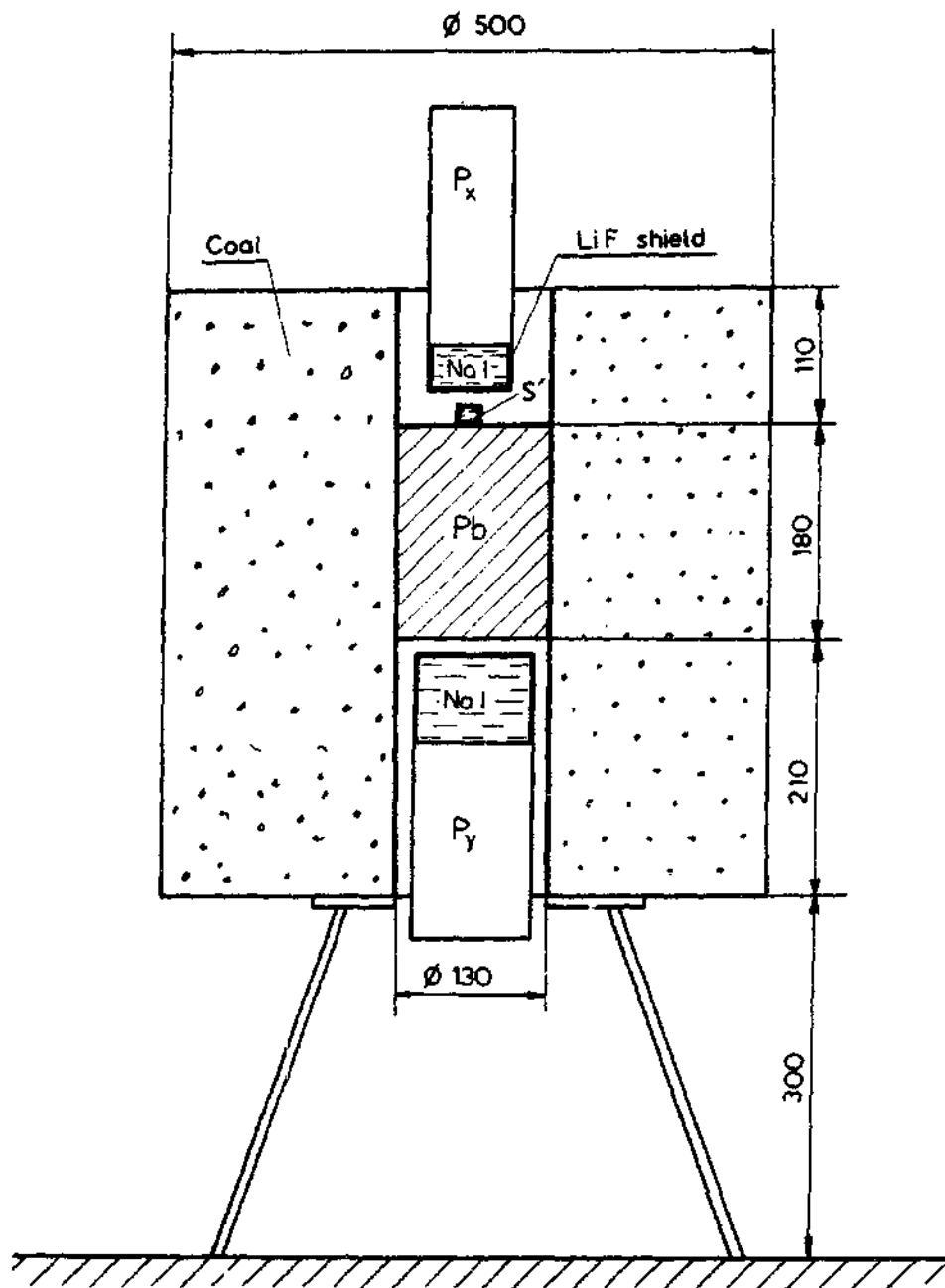


Fig. 6.

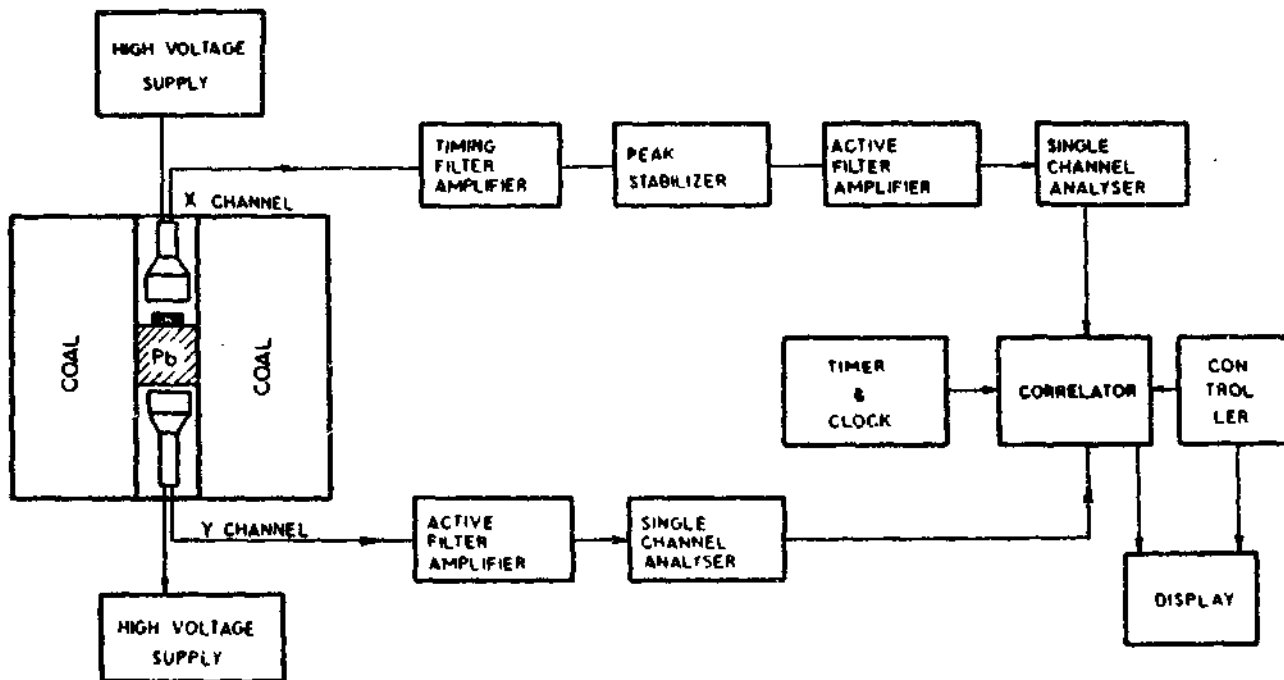


Fig. 7.

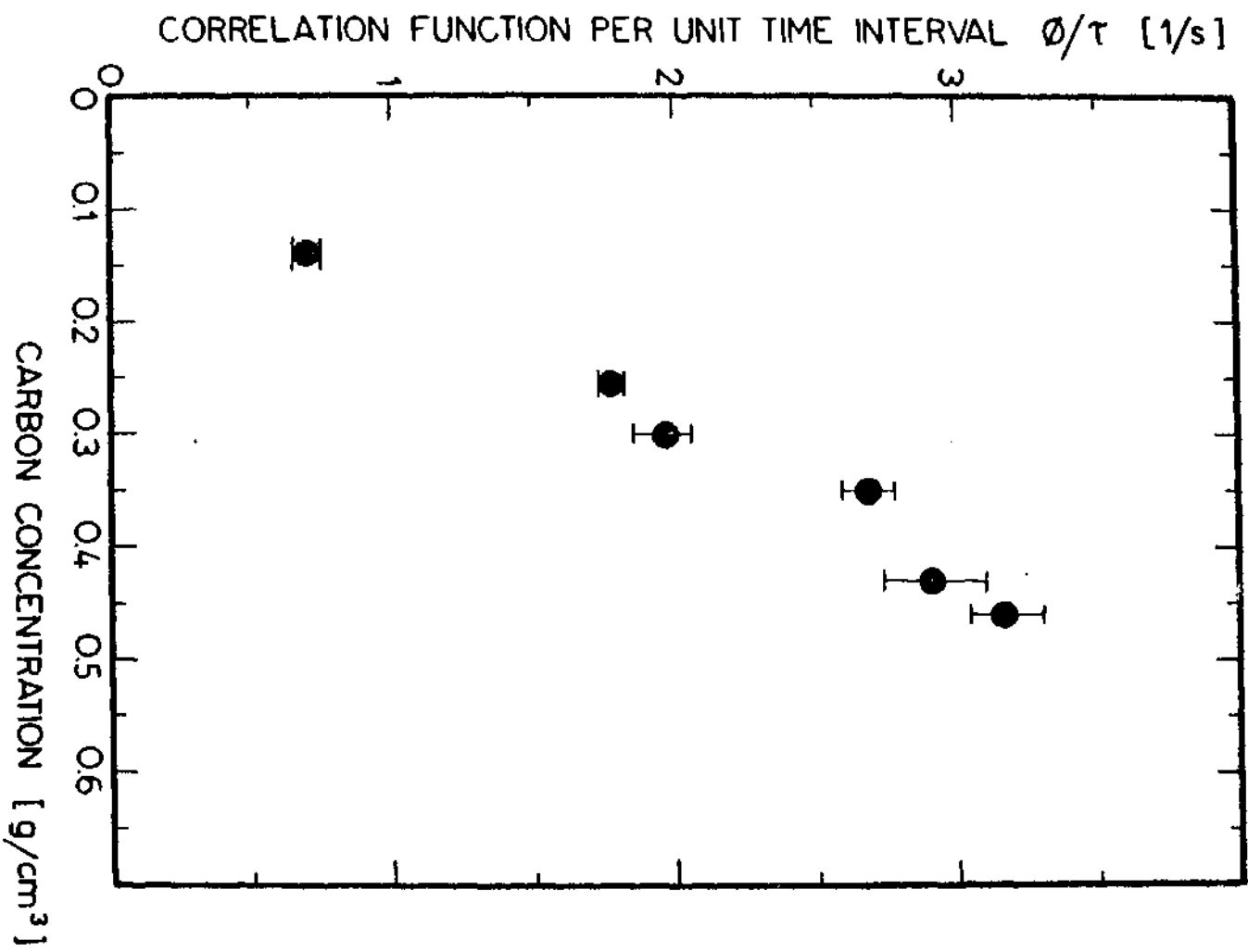


Fig. 8.