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Technical Report 11

By
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University Park, Pennsylvania

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Abstract

This report reviews some of the physical methods which have been and are being used to characterize coals in the Penn State/DOE program. These include maceral and reflectance analysis, density, various tests of the plastic behavior of coals, Vickers microhardness, and Hardgrove grindability. The ultimate objective of this program is the establishment of interrelationships between coal properties and industrial behavior.

Any characterization of coal, physical or chemical, is likely to be influenced by the petrographic heterogeneity of the particular sample. Further, the behavior of coal during pulverization, cleaning, and most industrial uses also depends upon the proportions and mode of occurrence of the various organic macerals and inorganic minerals. Variability in coal composition and behavior which is due to petrographic differences are modified by the extent to which the coals have been advanced in rank as a result of their thermal histories. Some of the direct methods of measuring petrographic composition and physical rank parameters are discussed.

Structural parameters such as aromaticity and the ring index can be derived from certain of the physical constants of coal. The results obtained in some earlier overseas studies are reviewed; no similar work on U.S. coals has been reported.

The thermoplastic behavior of some coals is controlled by both petrographic composition and rank. Its importance in carbonization is well established, and now it is possible to identify aspects of gasification and liquefaction technology which are influenced by these properties. The porosity and permeability of coals affects such properties and processes as methane adsorption and drainage, reactivity during gasification, and the production of chars.

The complexities of coal structure and behavior often have defied or complicated absolute quantitative analysis, and much of the conventional

characterization of coal still relies on established empirical testing. Renewed interest in the science of coal presents an opportunity to improve and extend our analytical techniques by taking advantage of new developments in other areas of science.

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Preface

The overall objective of The Pennsylvania State University's DOE program (Contract No. EX-76-C-01-2030) is the development of a capability to predict the behavior of coal in beneficiation, conversion, and combustion processes. To this end a comprehensive set of physical and chemical tests are being performed on 1300 samples selected so as to represent as nearly as possible the compositional range of U.S. coals. This report discusses some of the physical methods which are being used in this program to characterize coals, and their industrial relevance.

A specific task of the program is an investigation of the fluidity of coals in order to understand its possible influence in gasification and liquefaction processes. The Gieseler test which is being used in this research is discussed in the section dealing with the characterization of the plastic properties of coals.

I. INTRODUCTION

The principal purpose of this paper is to make a limited presentation of some of the results of the physical characterization of coal performed by the author and his colleagues in relation to established and future extraction, beneficiation and utilization processes. A second objective is to demonstrate how some of these properties can be used in physical constitution analysis in order to gain some insight into the basic structure of coal.

II. THE HETEROGENEOUS AND FLAWED NATURE OF COAL

Coal is not composed of the same mixture of materials throughout; the composition and texture of the mixes of organic macerals and inorganic minerals can vary not only between different coal seams, but also vertically and horizontally within individual seams. This heterogeneity of coal influences most of the physical properties dealt with here, and any analysis or test which does not compensate for this factor is likely to be less effective.

The procedures for measuring the maceral composition of a coal are well established (ICCP, 1963; ASTM, 1976e). A microscopic point-count technique is used to identify and record the coal macerals and, sometimes, minerals that are intersected in the course of a grid traverse across a polished surface of a coal block or pellet. With a statistically acceptable coverage, a volume percent analysis of the coal in terms of its petrographic constituents is obtained.

In general, a maceral analysis is often sufficient to relate petrographic composition to behavior in processes such as carbonization and liquefaction. However, the manner in which those materials are associated together provides an added dimension in consideration of physical properties and processes such as hardness and breakage. A sample in which the vitrinite occurs entirely in thick, homogeneous bands will be more friable than one in which that maceral is finely dispersed throughout the sample and intimately mixed with the other macerals. Associations of macerals in sizes greater than 50 μm are referred to as microlithotypes, and the proportions of these associations again are determined with established microscopic techniques (ICCP, 1963).

The physical properties of coal are complicated by the fact that layering of the coal and mineral constituents at the time of peat deposition, and changes resulting from the directed pressure of the rock overburden during subsequent burial, together impart an anisotropy of the physical properties. Consequently, some of the mechanical characteristics of coal can be different parallel and perpendicular to the bedding (Brown and Hiorns, 1963).

A further complication arises from the physical flaws which exist in coal, due in large part to the presence of bedding planes, and to the joints and cleats which are approximately perpendicular to the bedding.

III. DENSITY

The density of coal is a determinant of behavior in wet and dry methods of coal preparation, and a consideration in transportation and storage. Inasmuch as the density is an indication of pore volume, such measurements are relevant to methane content and drainage, water content, reactivity in gasification, and the porosity of chars produced from coal (Mahajan and Walker, in press).

Helium should have the most opportunity to penetrate pores, and for this reason measurement of density using this medium generally is regarded as the optimum method. However, there are closed pores in coals, and small and slit-shaped pores which are not available to helium (see Mahajan and Walker, *ibid.*). Helium density measurements are elaborate and time consuming. The apparatus employed must have high precision of volume measurement because the volumes involved are extremely small.

Both methanol and water have been used in pycnometric measurement of coal density. Water densities are often measured at 20 or 30°C, and correction to 4°C is necessary. Correction for the ash of the sample is often made, assuming an average specific gravity of the ash constituents of 3. Methanol values tend to be higher than helium densities (Tschamler and de Ruiter, 1963). With few exceptions, the values of water and helium densities reported by Ettinger and Zhupakhina (1960) showed excellent agreement. Also, Dulhunty and Penrose (1951) have determined water density values which were similar to the helium densities determined by Franklin (1949). Water densities of low-rank coals can be higher than helium densities, and lower values of water density of high-rank coals have been attributed to their hydrophobic character. Wetting agents have been used to aid penetration of water into coal pores (Ettinger and Zhupakhina, 1960).

Jones (1961a) has described a method which may be used for determining the density of small amounts of hand-picked coal macerals. In this, the refractive index of Thoulet's solution (aqueous potassium mercuric iodide) is measured at the point in a graded density column at which minus 60 mesh maceral particles are suspended as a band in a small hollow prism (Figure 1). This is accomplished with an optical goniometer and the minimum deviation method of refractive index determination in sodium light. The relationship between the refractive index and density of different concentrations of Thoulet's solution at the temperature of determination, once established, enables the density of the maceral to be calculated.

Prior to each determination, two small quantities of the maceral are evacuated in a vacuum desiccator in both distilled water and Thoulet's solution, using a small amount of dilute soap solution in each instance. In a series of determinations done by the author, five sets of readings upon each

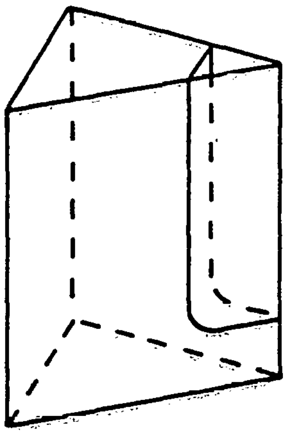

Figure 1. PRISM FOR MICRO-DENSITY DETERMINATIONS
(Modified after Jones, 1961a)

sample evacuated in the two solutions were made, and the difference in the averages of the two sets of results reflected the effect of the evacuating medium filling the pores in the maceral. This effect would be most marked in macerals with high porosities. The density of the coal as determined by this micro-density method may be calculated from equation (1) (Jones, 1961a).

$$\frac{d_s - d_{s_w}}{d_s - d_w} = \frac{d_{s_t} - d_{s_w}}{d_t - d_w} \tag{1}$$

where d_s is the true density of the sample,

d_{s_w} is the density of the sample after evacuation in water,

d_w is the density of water,

d_{s_t} is the density of the sample after evacuation in Thoulet's solution,

and d_t is the density of Thoulet's solution.

No correction for moisture was made to the micro-density values because it was not possible to determine the extent to which moisture was removed from the particles during evacuation. Any effect was likely to have been small because the purpose of evacuation was to fill the pores with liquid. Nor was any correction made for the effect of mineral impurities upon micro-density, because the vitrinite particles were ground sufficiently small for a band of pure vitrinite to settle out while any contaminated particles tended to sink. Jones (1961b) could not improve his results significantly by making such corrections.

The author measured the density of hand-picked vitrains by both pycnometric and micro-density methods. He found no pronounced difference between lower values from the two types of measurement in their relation with carbon content; however, for micro-densities exceeding 1.29 g/cm^3, the corresponding pycnometer densities are greater (Figure 2). For lower rank vitrinites the greater pycnometer densities lie farther from the curve of helium and water densities of vitrinites compiled from the results of various workers by van Krevelen (1961); for anthracites, however, the pycnometer densities are closer to this curve. There is no significant difference in density on correction for ash and moisture content of vitrinites of lower rank coals, although the corrected pycnometer densities of the vitrinites from anthracites are somewhat lower and in the same region as micro-density values. The low values of water densities compared to helium densities of high-rank coals has been referred to earlier.

IV. REFLECTANCE

Reflectance determinations have been judged to be the best single parameter of rank in coals of medium volatile bituminous rank or higher, and probably as good as other parameters for high volatile bituminous coals (McCartney and Teichmüller, 1972). Reflectance is the percentage of directly incident light which is reflected by a polished surface of the material under study. In the case of coal, reflectance usually is determined on vitrinite, with immersion oil as a medium, and in monochromatic green light of 546 nm. The particular advantages of reflectance measurement as an index of rank are that it is rapid, may be performed on relatively small amounts of sample, and, because a single homogeneous maceral is used, it is independent of the petrographic variability which can influence the results of chemical analysis.

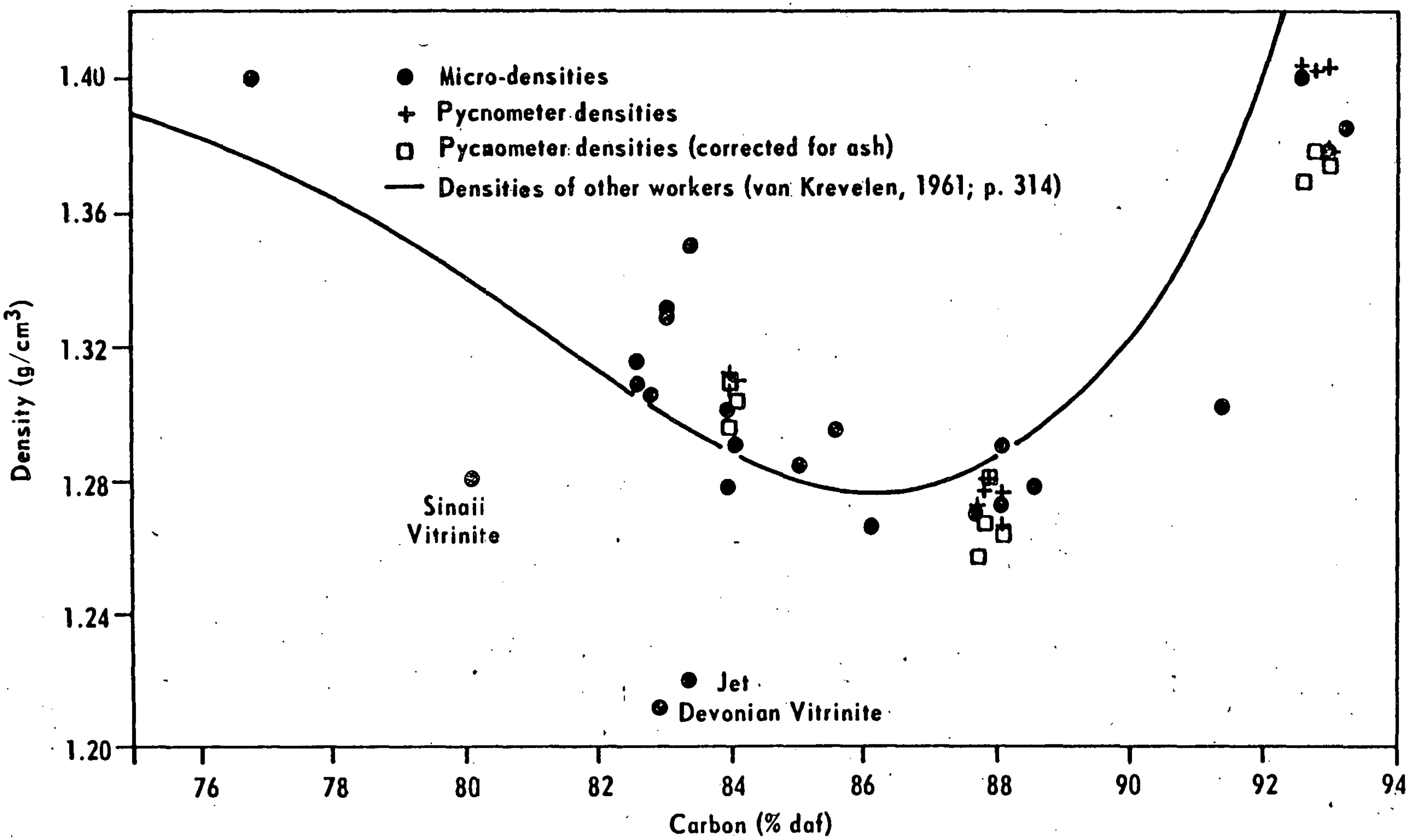

Figure 2. THE RELATION OF THE DENSITY TO CARBON CONTENT OF VITRINITES

The principal method used for determining reflectance employs a microscope photometer which measures the intensities of reflected light with a photomultiplier by comparison against a glass or mineral standard (ASTM 1976a; Davis, in press). A stabilized polarized light source usually is used, and because coal can be anisotropic, displaying maximum reflectance parallel to the bedding, it is a common procedure to rotate the microscope stage until the electric vector of the polarized light is parallel to the bedding. The average of a series of such readings (the mean maximum reflectance of vitrinite) is the most commonly determined optical parameter. Figures 3 and 4 show the relation of reflectance to carbon content and calorific value, respectively,of 390 U.S. coals. If reflectance is measured in two media (immersion oil and air are convenient), the maximum refractive index can be calculated from equation (2), and the maximum absorption index from equation (3).

$$n = \frac{\tfrac{1}{2}(n_o^2 - 1)}{\dfrac{n_o\ (1 + R_o)}{(1 - R_o)} - \dfrac{(1 + R_a)}{(1 - R_a)}} \qquad (2)$$

$$\kappa^2 = \frac{R_a\ (n + 1)^2 - (n - 1)^2}{n^2\ (1 - R_a)} \qquad (3)$$

where n is the refractive index,

κ is the absorption index,

$_a$is the measured reflectance of the vitrinite in air, expressed as a percent

$_o$is the measured reflectance of the vitrinite in oil, expressed as a percent

and n_o is the refractive index of the oil.

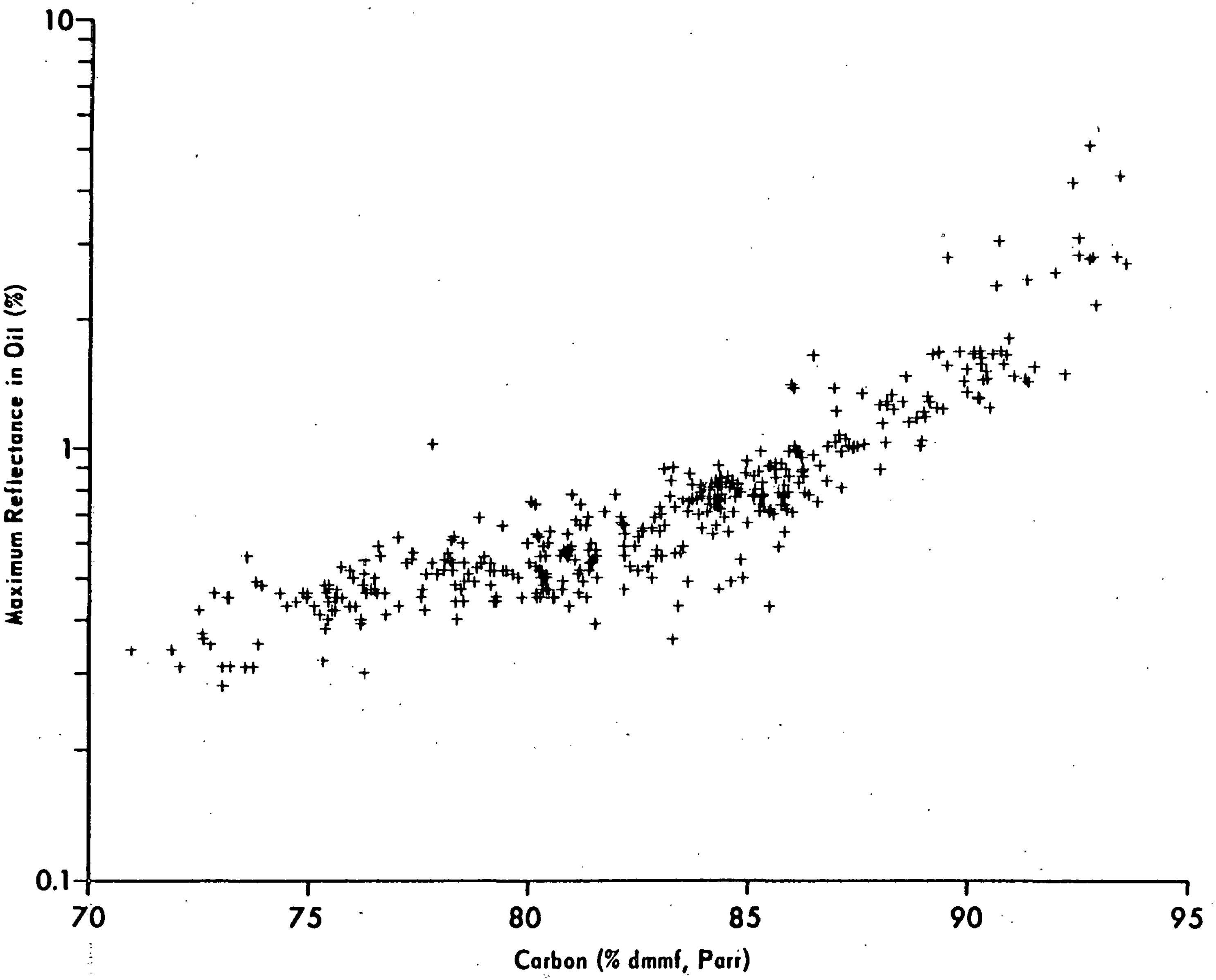

Figure 3. THE RELATION OF VITRINITE REFLECTANCE TO CARBON CONTENT OF U.S. COALS

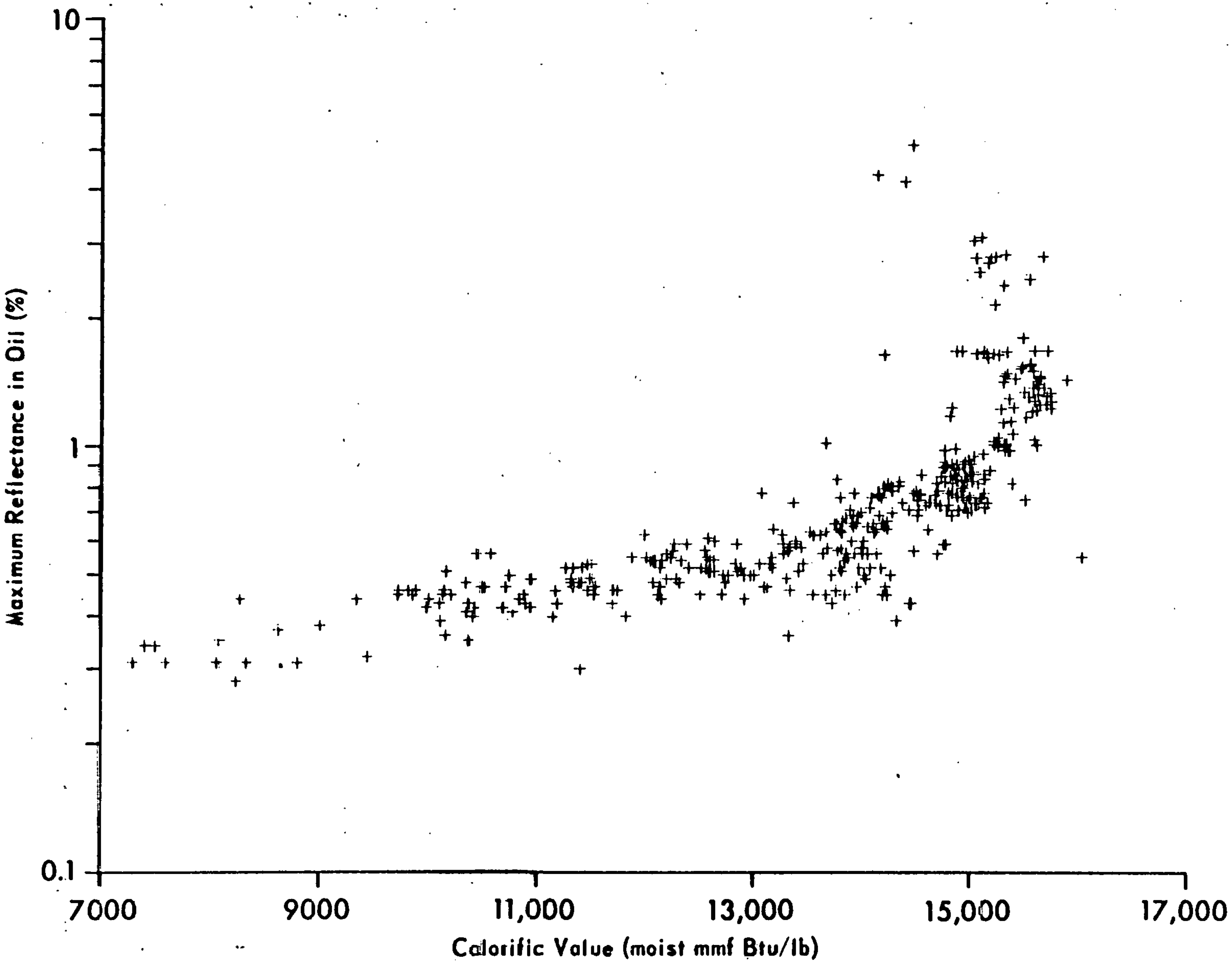

Figure 4. THE RELATION OF VITRINITE REFLECTANCE TO CALORIFIC VALUE OF U.S. COALS

The determination of the optical properties at different wavelengths (see Davis, in press) has enabled some inferences to be drawn regarding the variation in amount and complexity of aromatic structures in coals of different rank.

V. FLUORESCENCE MICROPHOTOMETRY

Figures 3 and 4 demonstrate that although reflectance is an effective parameter at high rank levels, it shows far less variation in the lower rank coals (especially lignites and subbituminous coals). However, in these coals the liptinite-group macerals (hydrogen-rich spore, resin and algal remains) fluoresce in blue and ultraviolet light (Ottenjann *et al.*, 1974; Spackman *et al.*, 1976). The peaks of fluorescence spectra of the spore remains (sporinite) shift from the range 400-500 nm for peats to the range 630-670 nm for high volatile B and A and medium volatile bituminous coals (Ottenjann *et al., ibid.*). This characteristic is the basis of a satisfactory means of rank differentiation.

VI. PHYSICAL CONSTITUTION ANALYSIS

van Krevelen has pioneered the methods of physical constitution analysis in coal science and most of this section is based on his and his co-workers invaluable contribution in this field, following successful application of the same principles in petroleum science (Vlugter *et al.*, 1935).

Coal is a complex mixture of chemical compounds and the application of its physical properties in the manner which will be described will give an average structure of the whole substance in terms of certain parameters. The physical constants chosen are those for which it has been possible to determine the contribution made by each type of atom to some function of that constant. Sometimes that function may be additive, when it is purely the sum of those contributions. At other times, there may be a discrepancy from the experimentally determined constant, and this discrepancy can be related to the structure of the coal "molecule." The term "molecule" here refers to mean structural unit rather than an actual molecule.

The additive relationship is expressed thus:

$$MF = C' \cdot \phi_c + H'\phi_h + O'\phi_o + \ldots\ldots + \Sigma X'\phi_{x_i} \qquad (4)$$

where MF is the additive function, expressed per mole,

M is the molecular weight,

X' is the number of structural factors of the i^{th} kind per mean structural unit,

ϕ_c, ϕ_h, etc. are the atomic and structural contributions to the additive function,

and C', H', etc. are the number of carbon, hydrogen, etc. atoms per mean structural unit, given simply by dividing the dry, ash-free ultimate analysis value by the atomic weight.

In the case of coal the molecular weight is not determinable, but the reduced molecular weight can be derived as shown later (equation (12)). For this reason equation (5), which follows from equation (4) is applicable here.

$$\frac{MF}{C'} = \phi_c + H'/C' \cdot \phi_h + O'/C' \cdot \phi_o + \ldots\ldots\ldots\ X'/C' \cdot \phi_x \qquad (5)$$

Given (1961) has pointed out that the assumption that certain properties are additive functions has no theoretical foundation because of intramolecular interaction, so that the method is both empirical and approximate. This is especially so in the case of aromatic compounds where the cyclicity and certain conjugations necessitate the use of additional parameters, although infrared studies have indicated that some of these structures are absent in coal and need not be taken into account. The atomic contributions themselves may not have been derived from suitable model substances, partly because of the difficulty of obtaining such data, so these may not be accurate. However, in spite of the assumptions made here and later, the method is of some value for the conclusions which may be drawn, particularly because van Krevelen and his co-workers have claimed consistency with results from other methods, such as x-ray analysis.

The procedure for employing molar refractivities now will be described in full and any criticisms of the steps involved will be-made at the end.

One of the important structural parameters is the aromaticity, f_a, defined as the ratio of the number of aromatic carbon atoms to the total number of carbon atoms per mean structural unit.

Thus: $f_a = C'_a/C'$

For a saturated hydrocarbon

$H' = 2\,C' + 2$

On the closing of a ring there are two less hydrogen atoms, and for each aromatic carbon atom that replaces a saturated carbon atom there is one less hydrogen atom. Thus:

$$H' = 2C' + 2 - 2R - C'_a \qquad (6)$$

where R is the number of rings per mean structural unit.

Dividing through by C'

$$2\,\frac{R-1}{C'} = 2 - f_a - H'/C' \qquad (7)$$

where $2\,\frac{R-1}{C'}$ is termed the ring condensation index.

When applying equation (7) to coal, the H'/C' ratio should be corrected for the presence of elements other than carbon and hydrogen. The assumption is made at this stage that the number of bridges in a polymeric substance such as coal which also would reduce the number of hydrogen atoms is small in relationship to the ring condensation index.

For large molecules, the ring condensation index may be taken as 2R/C', and equation (7) becomes:

$$f_a = (1 - H'/C') + (1 - 2\,R/C') \qquad (8)$$

The first of two methods to be considered here for determining f_a was developed by van Krevelen and Chermin (1954a) using molar volumes, and will be referred to as the Group Analysis method.

Traube (cited by Schuyer and van Krevelen, 1954) has given the molar volumes of liquids by equation (9).

$$V'_m = \Sigma_i\, n_i \cdot V_i - K_m + \emptyset_m \qquad (9)$$

where n_i is the number of atoms of the i^{th} kind per molecule,
V_i is the volume of these atoms per gram atom,
K_m is the molar volume contraction caused by structural factors,
and $\emptyset_m$ is the molar free space due to end groups, taken as a constant.

van Krevelen and Chermin believed that it is reasonable to apply this equation to vitrinite. They also assumed that K_m is determined only by the number of rings per mean structural unit and that the structural contribution of the rings to the molar volume (V_r) bears a linear relationship to the H'/C' ratio. Investigating this relationship for cellulose, polystyrene and graphite enabled the following equation to be developed.

$$V_r = 9.1 - 3.65\ H'/C' \qquad (10)$$

If Traube's atomic volumes are introduced at this stage and $\emptyset_m$ neglected, equation (9) now may be restated as

$$V_m = \frac{M}{d} = 9.9\ C' + 3.1\ H' + 3.75\ O' + 1.5\ N' + 14\ S' - (9.1 - 3.65\ H'/C')R \qquad (11)$$

The molecular weight, M, cannot be determined for coal, but the reduced molecular weight or molecular weight per gram atom of carbon $M_c = M/C'$ is given by

$$M_c = 12 + H'/C' + 16\ O'/C' + 14\ N'/C' \qquad (12)$$

where the contribution of sulfur is neglected.

Hence,

$$\frac{1}{d} = \frac{9.9 + 3.1\ H'/C' + 3.75\ O'/C' + 1.5\ N'/C' - (9.1 - 3.65\ H'/C')R/C'}{12 + H'/C' + 16\ O'/C' + 14\ N'/C'} \qquad (13)$$

from which R/C' and thus f_a can be calculated.

The second method of determining the aromaticity to be considered here is called the Graphical Densimetric method (van Krevelen and Chermin, 1954b), and seems to be more favored than the one previously described (Leicester, 1956; Dryden, 1964). In it, linear relationships between the molecular volumes and H'/C' ratios of model substances of known aromaticity are used. This information, represented graphically, enables values of f_a for vitrinites to be read off, knowing their M_c/d and H'/C' ratios, corrected for the presence of "foreign elements" such as oxygen, nitrogen and sulfur. Assuming the principal types of functional groups in which th se elements occur, and assigning values for the corrections needed for these groups,

$$\left(\frac{M_c}{d}\right)_{corr} = \left(\frac{M_c}{d}\right)_{exp} - (8.1\ O'/C' + 6.4\ N'/C' + 1.25\ S'/C') \quad (14)$$

can be applied for the molecular volumes of vitrinite per carbon atom. No similar formula has been developed by van Krevelen for correcting the H'/C' ratio, but correction terms exist and can be used if the concentrations of certain functional groups are known or assumed. van Krevelen *et al.* (1957) later added data derived from pitch fractions and further model substances to improve the method. Their graph for obtaining f_a values for vitrinite has been reproduced as Figure XVI, 4b in van Krevelen (1961). In the Graphical Densimetric method, R/C' is calculated from f_a using equation (8).

Schuyer and van Krevelen (1954) cited L.V. Lorenz and H.A. Lorentz as having defined the molar refraction of an organic compound thus:

$$R_m = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d} \quad (15)$$

where n is the refractive index of the coal. They have used equation (16) to derive the arithmetic mean of refractive indices.

$$n = \sqrt{\frac{(n^2{}_{min} + 2\ n^2{}_{max})}{3}} \quad (16)$$

van Krevelen and Schuyer (1957) and van Krevelen (1961) have given incorrect versions of this equation.

Unlike the molar volume, the refractivity is not a simple additive function, for ϕ_X in equation (5) is not constant but a function of C'_a if $X = C'_a$, that is

$$(\phi_{C'_a})\ \text{refr.} = \phi\ (C'_a) \quad (17)$$

Equation (5) may therefore be applied as

$$Rm/C' \text{ (exp)} = R_c + H'/C' \, R_h \ldots\ldots + f_a \, \phi \, (C'_a) \tag{18}$$

where R_c etc. are the atomic refractions for carbon, etc.

The difference between the experimental and calculated molar refractions, probably due to double and triple bonding, termed the molar refractometric increment, is defined by

$$I_m = R_m \text{ (exp)} - R_m \text{ (calc)} \tag{19}$$

and therefore

$$I_m = C'_a \, \phi \, (C'_a) \tag{20}$$

Using the atomic refractions of 2.558 and 1.039 for carbon and hydrogen, respectively, as determined by Wibaut and Langedijk (cited by Schuyer and van Krevelen, 1954), and average atomic refractions of 1.65, 2.48 and 7.64 for oxygen, nitrogen and sulfur, respectively, as determined by Vogel *et al.* (cited by Schuyer and van Krevelen, *ibid.*), one may arrive at R_m/C' (calc) and, hence, at the molar refractometric increment per aromatic carbon atom

$$I_m/C'_a = 1/f_a \, (R_m/C' \text{ (exp)} - R_m/C' \text{ (calc)}) \tag{21}$$

Schuyer and van Krevelen (*ibid.*) have shown that there is an ambiguous relationship, between I_m/C'_a and the aromatic surface area, S^{*}. This theoretical relationship, which they have confirmed with experimental data on model substances is shown graphically in Figure XVII, 13 of van Krevelen (1961). From the graph, S^x can be derived for vitrinites, and hence, from equation (22) (Schuyer and van Krevelen, 1954)

$$S^x = 2.46C'_a \text{ Å}^2 \qquad (22)$$

the number of aromatic carbon atoms per mean structural unit can be calculated. Finally, using values of f_a and R/C', determined by either Group Analysis or Graphical Densimetric methods, the total number of carbon atoms and number of rings per mean structural unit can be calculated.

These methods which involve the use of molar refractions have been used by Schuyer and van Krevelen (1954), Leicester (1956), Bond *et al.* (1958), and Davis (1965) to arrive at an understanding of the basic structure of vitrinites. Leicester used refractive indices calculated by Cannon and George (1944) at 7000 Å which are not strictly compatible with the atomic refractivities determined at lower wavelengths. Schuyer and van Krevelen and Leicester used density values read from an established curve relating density to carbon content, while Bond *et al.* used original helium density values. Davis used pycnometer densities and micro-density values measured using the method of Jones (1961a). Bond *et al.* and Davis also have applied the same methods to data obtained from carbonized coals.

van Krevelen's densimetric and refractometric methods have been criticized by Dryden. The arguments for and against will now be considered. Dryden and Griffith (1953) developed a method of calculating the number of rings per mean structural unit (R) from values of 2 R/C' determined by van Krevelen using his densimetric method. It is not necessary to consider the details of the method here, but the values which Dryden (1955) obtained do not differ appreciably from those derived by van Krevelen using his refractometric method. Dryden, however, has not favored the use of densities for arriving at structural parameters, because of the unknown relationship between the molecular packing of coals and that of the reference model substances.

In a method for comparing data from different sources on the chemical structure of coals, Dryden (1958) observed that the choice of the best available results is important, because of the chemical implications of such values as the number of fused aromatic rings in a cluster. Whereas previous methods of understanding coal structure have involved the derivation of two parameters, one from a ring number group (eg. C'_a) and one from the aromaticity group (eg. f_a), Dryden has developed a means of using experimental data from one source only. This is important because of the possibility that data from two sources may be incompatible.

The chief argument seems to surround van Krevelen's assumption in the derivation of equation (7), that the number of bridges involved is small compared to the number of rings per mean structural unit. Its omission, Dryden claimed, would lead to "meaningless values" of the parameters calculated. Equation (7) should, in fact, read

$$2(R - 1)/C' = 2 - f_a - (H'/C') - (B/C') \qquad (23)$$

where B is the average number of bridges between mean structural units. This equation, however, was abandoned by Dryden in a method which replaces aliphatic chains and direct links between carbon atoms of adjacent nuclei in a correction which he claimed converted the structure to an equivalent hydrocarbon. Use of this method requires only ultimate chemical analysis and Dryden's graphs for certain mathematical properties of model substances.

The estimation of certain properties by this method and variation of the assumptions involved enabled Dryden to compare the individual methods of arriving at structural parameters. The densimetric method gives low values of R_a (the number of fused aromatic rings per mean structural unit) and high values of f_a, whereas the refractometric method gives values of R_a which are too high and of f_a which are too low. Dryden observed that small differences in f_a can be important in estimating the size of ring clusters.

Dryden also took up Given's concern (1961) about the difficulty in choosing reference substances. He pointed out that the choice of appropriate polycyclic aromatic compounds and determination of their refractive indices is difficult and complicated by their anisotropy.

A number of assumptions are involved in Dryden's method to which van Krevelen (1959) has taken exception. One of them was a value for B of 2.25, which might in fact vary with rank. Dryden's view was that such variation is likely to be small. Another assumption that has been made involves the relative concentration of oxygen groups, but which Dryden again claimed is not critical.

van Krevelen clarified his original statement on equation (7) as follows. If it cannot be demonstrated that B/C' is negligibly small, then the calculated value of the ring condensation index, which can be experimentally determined as $(2 - f_a - H'/C')$, would be considered as an average for the whole "molecule". He then demonstrated how this value does give a measure of the number of rings per average structural unit. van Krevelen also challenged Dryden's statement that the densimetric and refractometric methods are shown to give inferior values of parameters compared to x-ray, infra-red and nuclear magnetic resonance. The argument as to the relative merits of these different methods need not be considered here. In his response to van Krevelen, Dryden (1959) admitted that his statement that neglect of B/C' in equation (7) leads to meaningless results may be only a half-truth.

Referring to this controversy, Given (1961) stated that, although the validity of Dryden's methods may be questioned on the grounds of the assumptions made, it appears that incorrect assumptions were made in the densimetric and refractometric methods. It is interesting to note that Given has calculated that the coal model which he has proposed would have a refractivity close to that of coal, but, whereas the model has only about two fused rings per cluster unit, the refractometric method leads to significantly higher values.

van Krevelen (1961) has observed that values of I_m/C'_a, after an initial increase with rank, show a decrease after about 90 percent carbon. This is explained as being due to charge transfer during stacking of lamellae. If the number of lamellae increases at the same time as there is an increase in the aromatic surface area S^*, so will there be an decrease in I_m/C'_a (see Figure XVII, 14, van Krevelen (1961)).

In spite of van Krevelen's proviso that his method may apply only for low-rank coals, it has been applied to all ranks and to carbonized coals. Bond *et al.* (1958) obtained similar results for carbonized as for untreated coals, and they suggest that the explanation offered for the anomolous results of high-rank coals might apply also for carbonized coals, with the size of aromatic clusters in both systems being similar.

Dryden (1964) has said that he expects equation (11) to be applied less accurately for carbonized coals because their structures are less mixed and somewhat more ordered, microcrystalline and with more condensed aromatics, so that they are further from the model substances used as the bases for the atomic increments. Because the atomic increments used in calculating R_m/C' (calc) are estimated for amorphous or fluid phases, Dryden (*ibid.*) believes that they may not be strictly applicable to carbonized coals with a greater amount of spatial order.

In conclusion it must be emphasized that Dryden's method (1958) is effectively a test of the various experimentally determined structural parameters and requires that one of the parameters be derived by each method under test. Dryden's objections to the assumptions involved in the densimetric and refractometric methods and his conclusion that there are other methods which will give more accurate estimates of the structural parameters do not invalidate them. They still are of value because of the limited availability of highly specialized data necessary for comparisons of structural parameters of coals. Dryden himself has been involved in such a study (Bond *et al.*, 1958) in which parameters derived by the densimetric and refractometric method were determined for carbonized coals.

Physical constitution analysis parameters have been calculated by the author for a series of samples, mainly of British coals, on which density, maximum and minimum reflectance determinations in air and oil,and ultimate chemical analyses had been done. Two sets of data have been calculated, one by the Group Analysis method and the other by the Graphical Densimetric method. In Figures 5 and 6 the aromaticity (f_a) determined by these methods is plotted against carbon content. The least spread occurs in Figure 6 which is based upon the Graphical Densimetric determination of f_a. Also plotted in this figure are the results obtained by van Krevelen (1961) and Leicester (1956). van Krevelen's data show a good linear relationship which has not been obtained with the present series of results. The author's values are mostly intermediate between those of van Krevelen and Leicester.

Figures 7 and 8 support the idea expressed by Mackowsky (1961) and McCartney and Teichmüller (1972) that reflectance is fundamentally related to aromaticity. One point, for a jet, which was notably displaced when reflectance

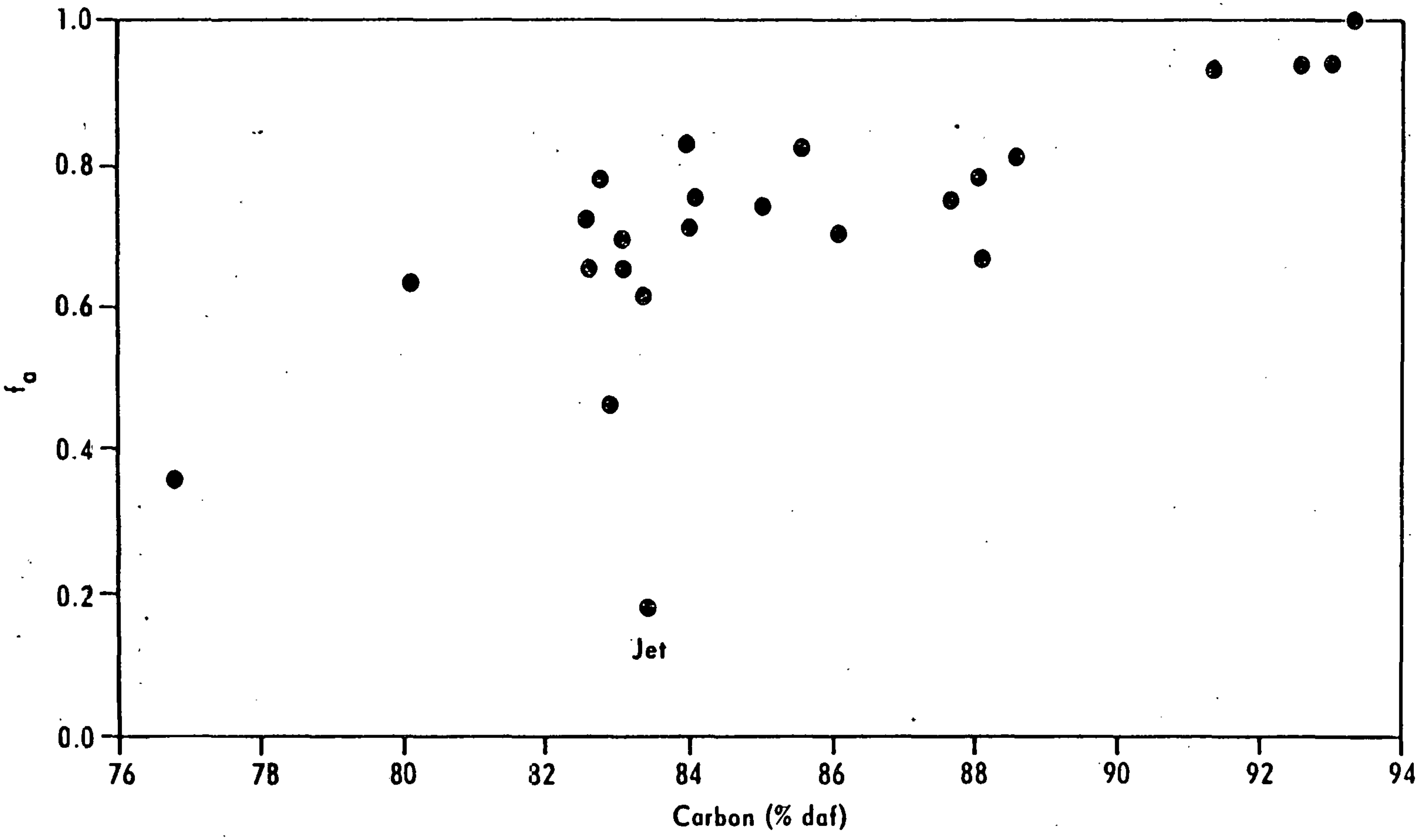

Figure 5. THE RELATION OF AROMATICITY (f_a) BY THE GROUP ANALYSIS METHOD TO CARBON CONTENT OF VITRINITES

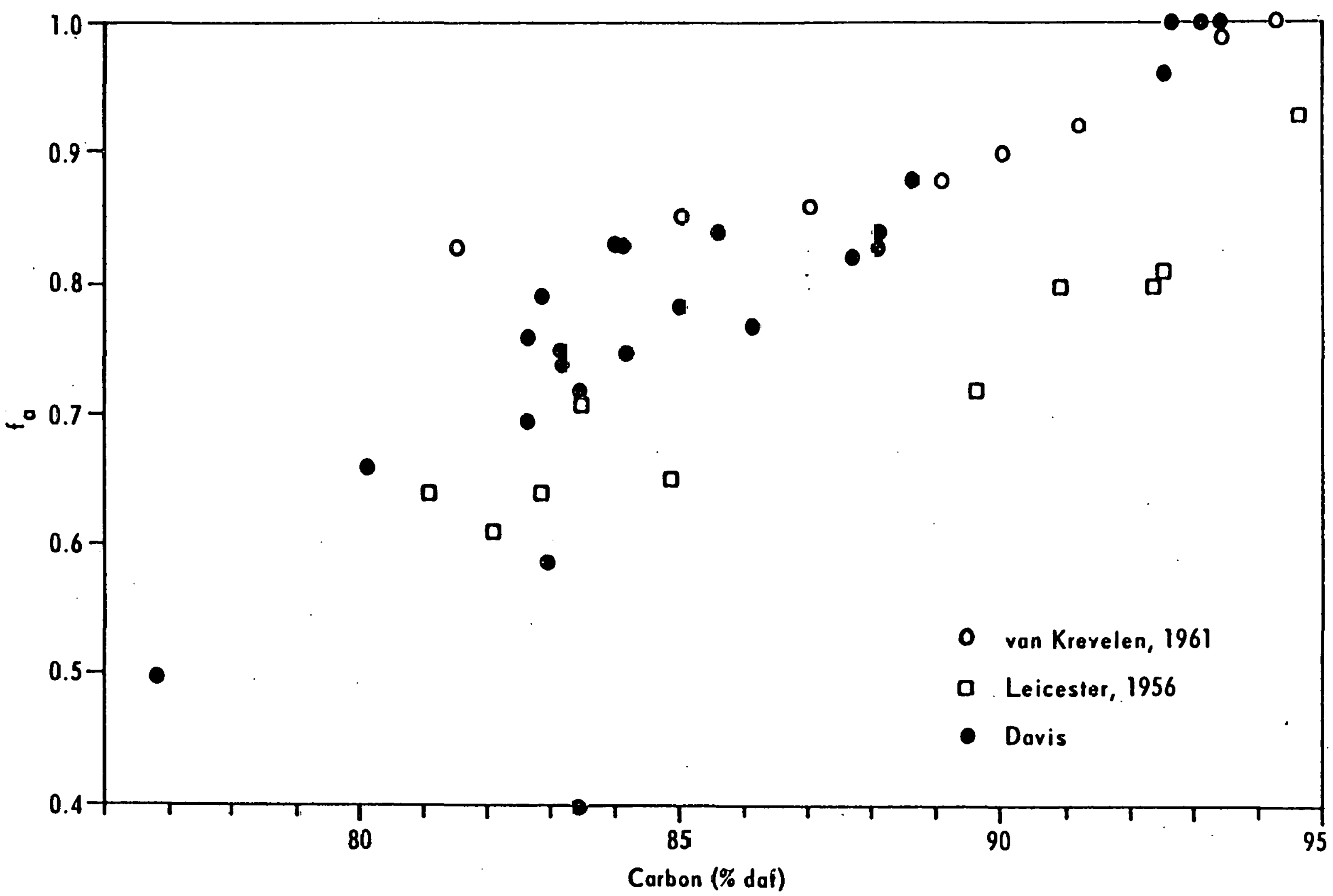

Figure 6. THE RELATION OF AROMATICITY (f_a) BY THE GRAPHICAL DENSIMETRIC METHOD TO CARBON CONTENT OF VITRINITES

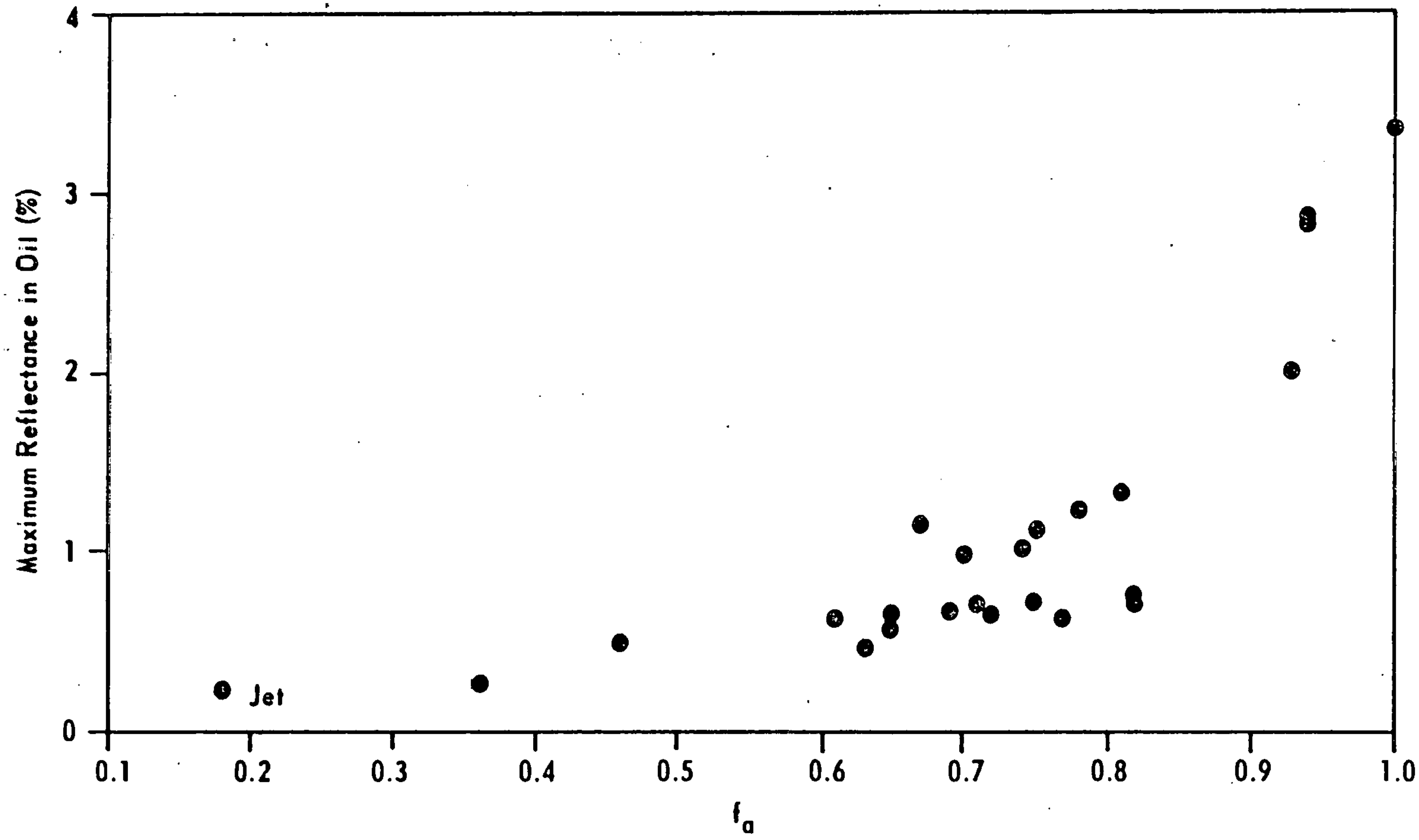

Figure 7. THE RELATION OF AROMATICITY (f_a) BY THE GROUP ANALYSIS METHOD TO REFLECTANCE OF VITRINITES AT 532 nm

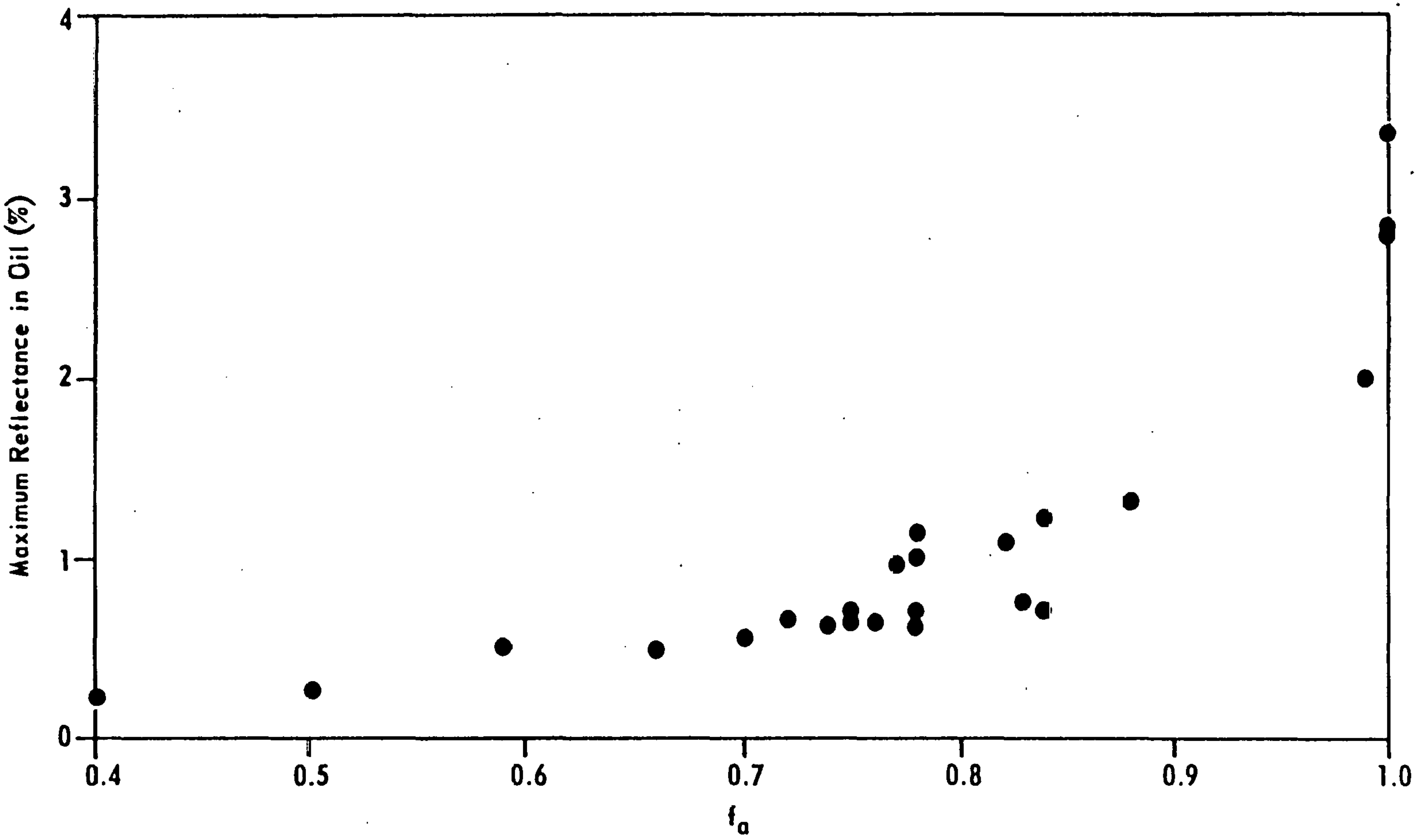

Figure 8. THE RELATION OF AROMATICITY (f_a) BY THE GRAPHICAL DENSIMETRIC METHOD TO REFLECTANCE OF VITRINITES AT 532 nm

is plotted against carbon content is not displaced on the reflectance against aromaticity curve; this sample has both a low reflectance and aromaticity, but a carbon content of 83.4 percent.

Figure 9 presents the Ring Indices derived by the Graphical Densimetric method. It also contains the results of van Krevelen (1957; 1961) and Leicester (1956). van Krevelen's 1957 data and Leicester's values were derived in a similar manner to those of the author. van Krevelen's results over most of the range of carbon content are somewhat lower than the present values, but they do show a minimum R/C' of 0.02, whereas Leicester's demonstrated an almost linear increase with rank. In 1961, van Krevelen was able to apply revised corrections to his H'/C' values for various oxygen-containing functional groups and, like Leicester, obtained an overall increase of R/C' with rank, but with a more rapid increase for the higher ranks. Dryden and Griffith (1955) also failed to obtain a minimum with their ring condensation indices derived from calorific values of coals.

The R/C' values for higher rank vitrinites obtained by the author lie close to both sets of van Krevelen's results in Figure 9, but the lower rank vitrinites seem to indicate a rise in the ring indices for progressively lower ranks. Even so, the high values of R/C' in this region are not higher than those of Leicester, although they have departed significantly from the two curves of van Krevelen.

Values of I_m/C'_a are plotted in Figure 10 and confirm the findings of van Krevelen and Leicester in that experimental results show a maximum at about 89 percent carbon, although theoretically the refractometric increment should increase progressively with rank. The explanation offered (van Krevelen and Schuyer, 1957; Leicester, 1956) for this phenomenon is that charge transfer forces bring about cohesion of lamellae into crystallite complexes.

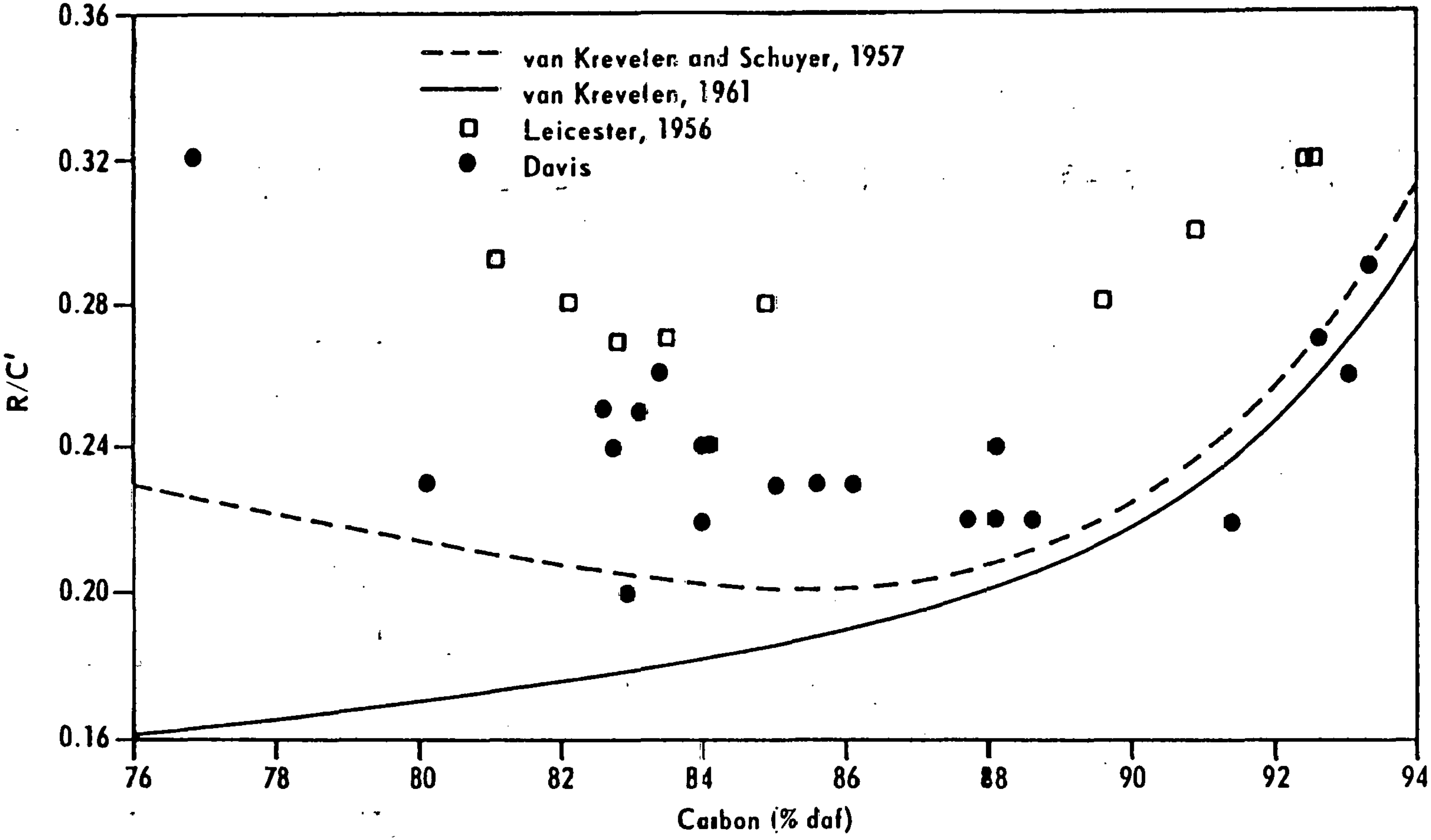

Figure 9. THE RELATION OF THE RING INDEX (R/C') BY THE GRAPHICAL DENSIMETRIC METHOD TO CARBON CONTENT OF VITRINITES

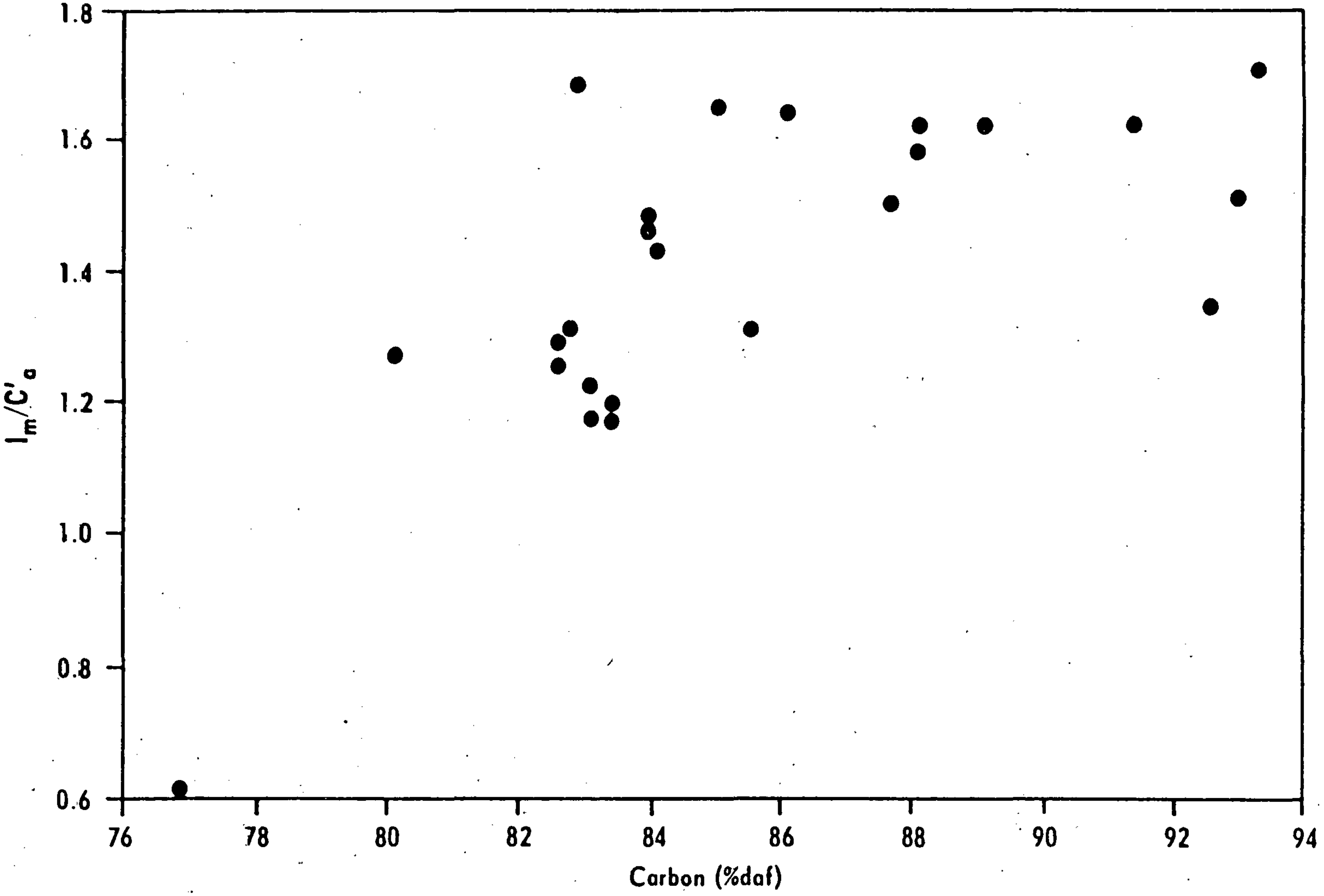

Figure 10. THE RELATION OF THE MOLAR REFRACTOMETRIC INCREMENT PER GRAM-ATOM OF AROMATIC CARBON (I_m/C'_a) TO CARBON CONTENT OF VITRINITES

In Figure 11 apparent values of $100/S^x$ are plotted against values of 100-C. The low-rank vitrinites do not lie close to van Krevelen's line for such materials (1961). Those which lie above the line are Northumberland and North Durham coals and a jet. With increasing rank the vitrinites approach the line, cross it at about 83 percent carbon and then swing up to approach the line again in the region of the higher reflecting bituminous vitrinites. With further increase in rank above about 86 percent carbon, the results are in close agreement with those of van Krevelen and demonstrate the rise in $100/S^x$ which marks the departure from the idealized straight line towards the origin.

Because C'_a, the number of aromatic carbon atoms per mean structural unit, is a simple function of S^x, estimations of this quantity by the refractometric method will give a maximum at a carbon content in the range 86-90 percent as demonstrated by Figure 12. Likewise, values of C', the number of carbon atoms per mean structural unit, show a poorly defined maximum of about 32 in Figure 13.

When van Krevelen and Schuyer (1957) and Leicester (1956) determined values of C'_a and C' for higher rank vitrinites, they did so using the idealized straight line that related $100/S^x$ to 100-C and passed through the origin, interpolating for coals which showed diverging values of $100/S^x$. They observed at that time that such a method was highly empirical and van Krevelen has since ceased to employ it. The values of C'_a and C' for higher rank vitrinites obtained in the present work are undoubtedly incorrect because they do not show a progressive increase with rank.

Figure 14, in which R, the number of rings per mean structural unit, is plotted against carbon content, shows a very wide spread of results. Although

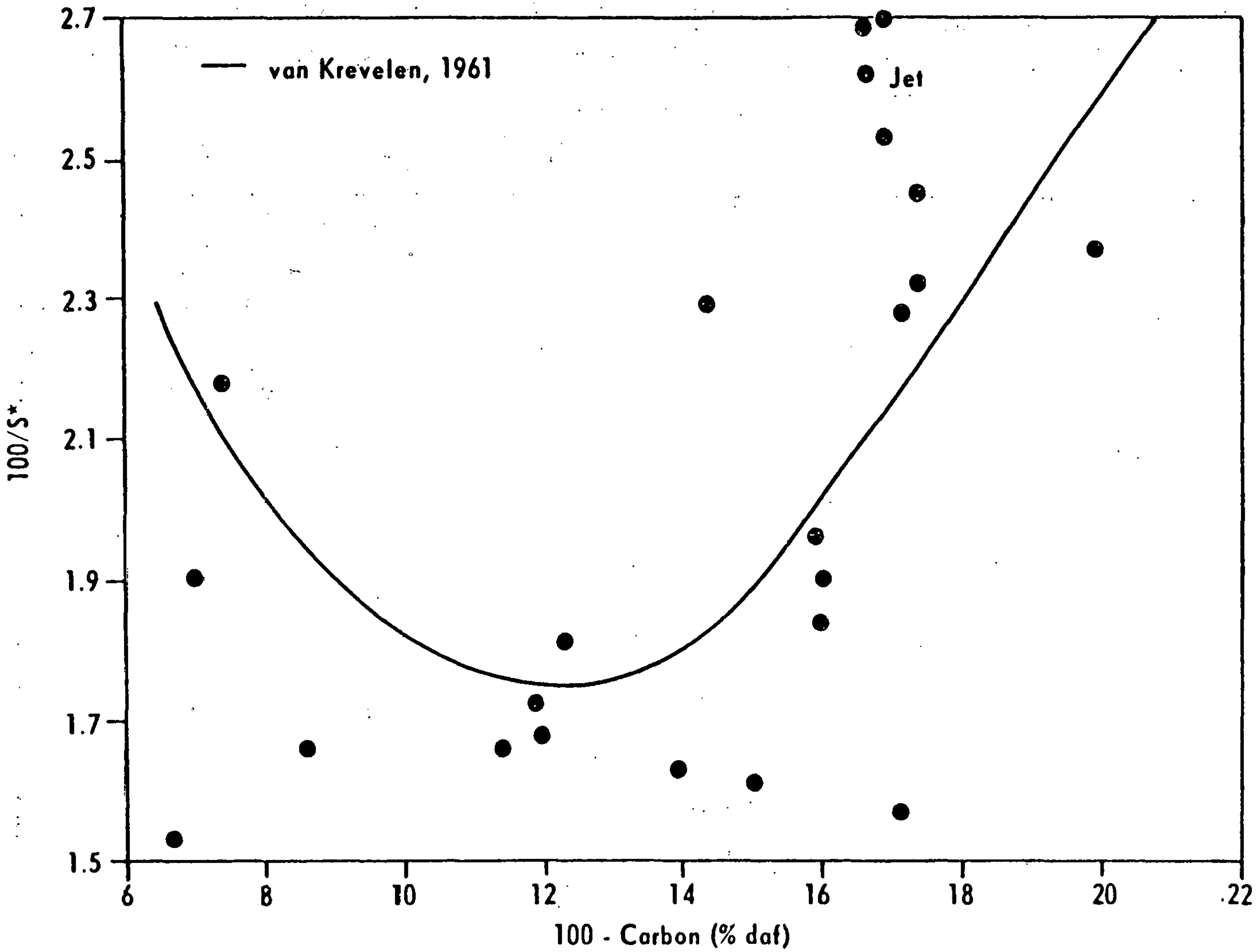

Figure 11. THE RELATION OF THE AROMATIC SURFACE AREA (S*) BY THE GRAPHICAL DENSIMETRIC METHOD TO CARBON CONTENT OF VITRINITES

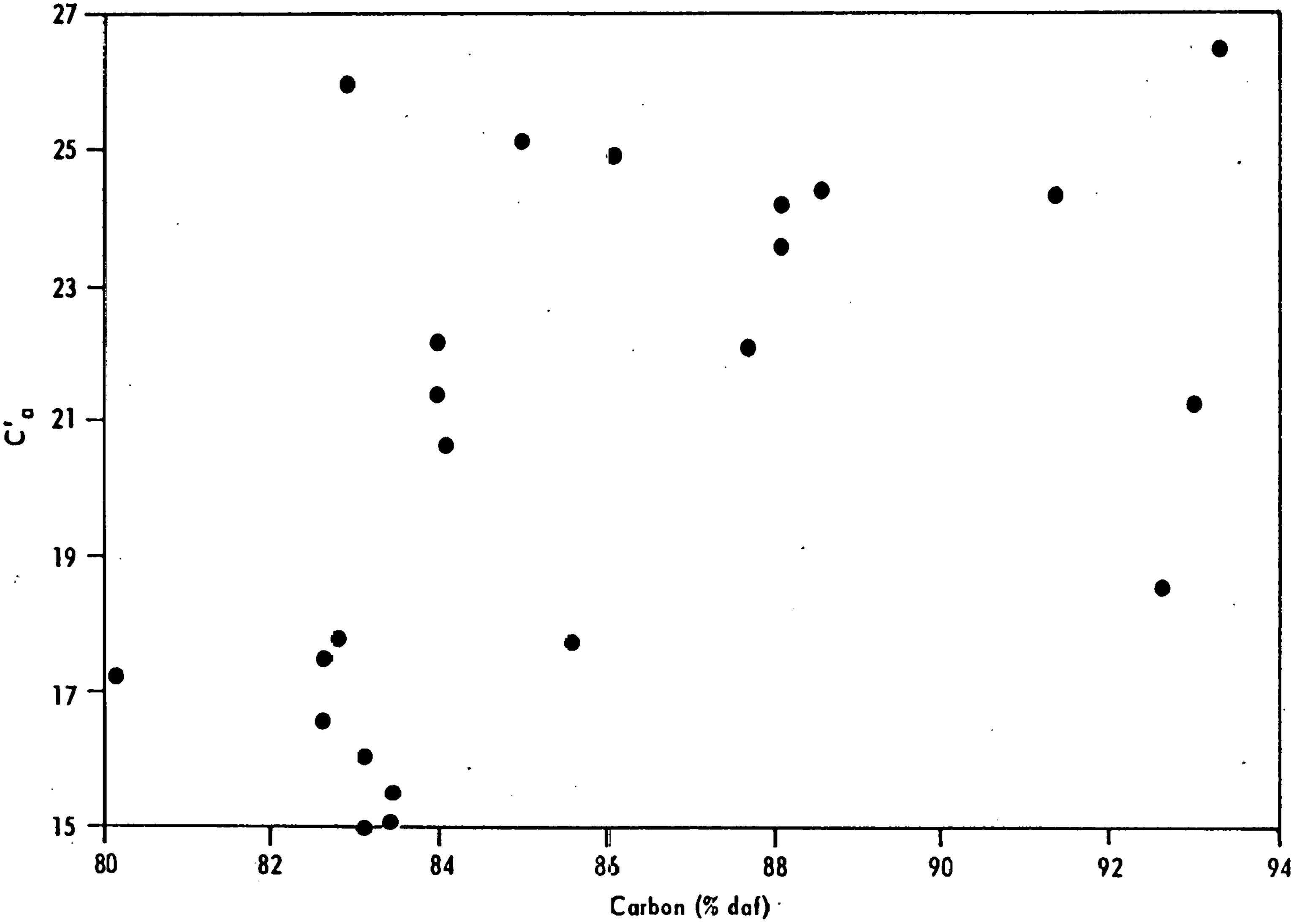

Figure 12. THE RELATION OF THE NUMBER OF AROMATIC CARBON ATOMS PER MEAN STRUCTURAL UNIT (C'_a) TO CARBON CONTENT OF VITRINITES

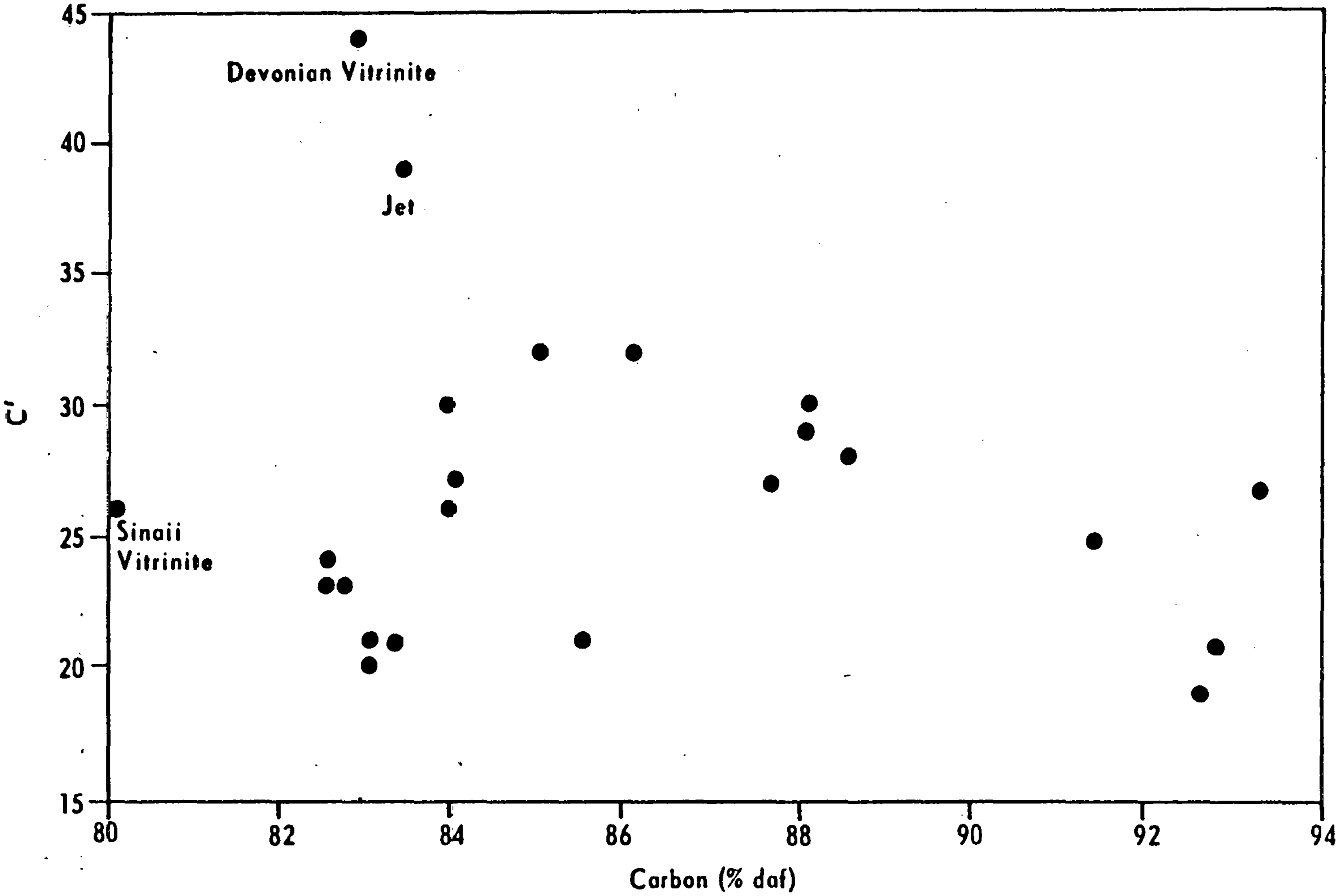

Figure 13. THE RELATION OF THE NUMBER OF CARBON ATOMS PER MEAN STRUCTURAL UNIT (C') TO CARBON CONTENT OF VITRINITES

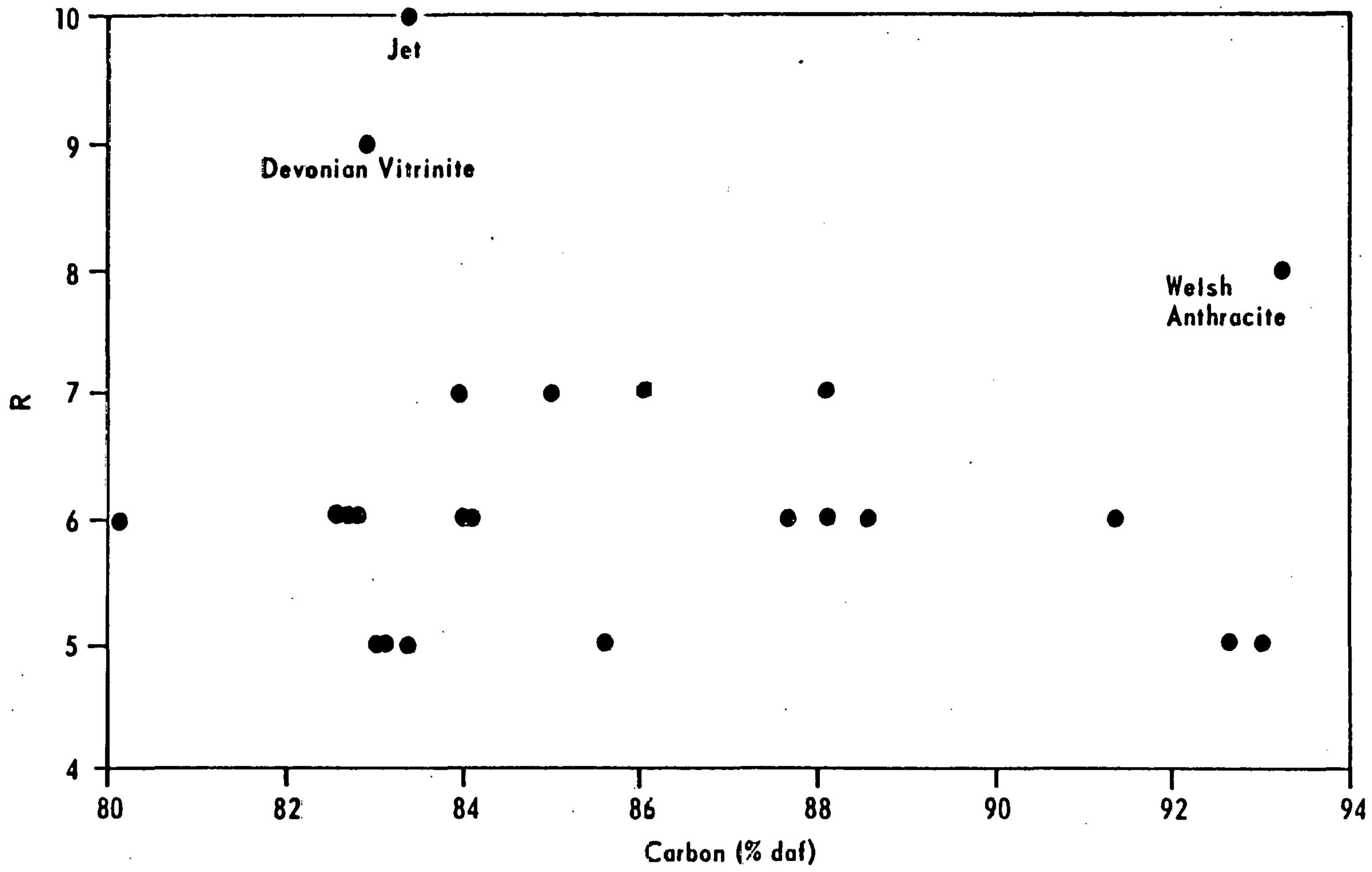

Figure 14. THE RELATION OF THE NUMBER OF RINGS PER MEAN STRUCTURAL UNIT (R) TO CARBON CONTENT OF VITRINITES

a maximum of about seven rings can be detected (somewhat more than has been interpreted from wide-angle x-ray diffraction profiles), unusually high results were obtained for one of the anthracites, a jet and a Devonian vitrinite.

VII. PLASTIC PROPERTIES OF COAL

Coals within the bituminous range of coal rank tend to be thermoplastic. The optimum development of these properties occurs within the ranges of about 88-89 percent carbon and about 25-30 percent volatile matter (Figure 15). The importance of the quantitative measurement of the plastic behavior of coal has long been recognized by those involved in the assessment of coals for coking purposes. To this end, a variety of techniques ranging from the childishly simple to the ingeniously complicated have been devised; these include the free swelling index, Gray-King coke type, Roga index, the microscope hot stage, and a variety of penetrometer, dilatometer and plastometer tests. Some of these will be described briefly in this section.

A. Free Swelling Index

This test quantifies the plastic behavior of coal when a 1-g sample is rapidly heated in a small crucible to 820°C in 2-1/2 min. The cross-sectional profile of the resulting coke button is compared to standard profiles numbered from 1 to 9 in half units.

Although intended primarily to provide some indication of the caking and swelling behavior of coal under the rapid heating of combustion processes, the test is often used as a very rough method of assessing the potential of coal for metallurgical coke making. The test is highly empirical, and the size and the shape of the crucible, the heating rate, and other test details have been carefully specified (ASTM, 1976b). Results can be invalidated by too fine a size consist of the coal sample, or too high a temperature gradient from bottom to top of the crucible (Proudfoot, 1971).

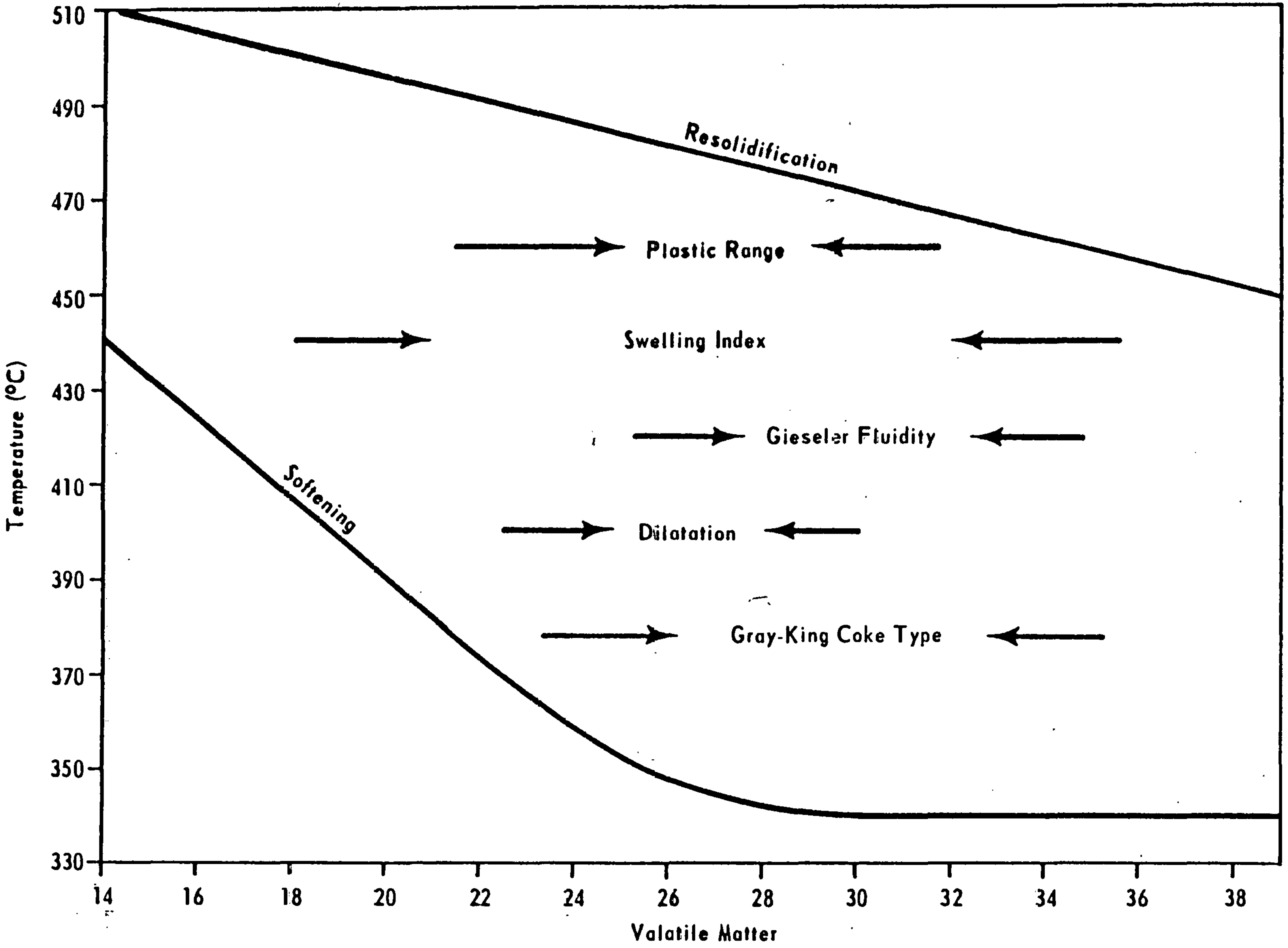

Figure 15. VARIATION IN THE PLASTIC PROPERTIES OF COAL WITH VOLATILE MATTER (Data from Loison et al., 1963)

B. Gray-King Coke Type

This test (British Standards Institute, 1959) differs from the previous one in that the rate of heating is lower (5°/min; from 300-600°C) to approximate more closely the conditions in a coke oven. The retort is a horizontal glass tube of about 2 cm diameter, and the charge consists of 20 g of minus 60 mesh coal. Again the profile and coherency of the coke pencils are visually matched against a series of standards. Gray-King cokes which are not swollen are classed from A to G, as follows:

A - pulverulent
B - just coherent, breaks to powder on handling
C - coherent, but friable if rubbed
D - shrunken, moderately hard
E - shrunken and fissured, hard
F - slightly shrunken, hard
G - hard, occupying the same volume as the original coal

If the coal is strongly caking, and the pencil has a volume greater than that of standard coke G, further tests are run to determine the number of parts by weight (x) of inert electrode carbon which must be added as a diluent to (20-x) parts of coal to give a standard coke G. The number of parts of diluent required is indicated as a suffix, as for example in G_9, the index for a strongly swelling coal. The relation between coke type and rank of a series of U.S. coals is illustrated in Figure 16. The large amount of scatter is due in large part to the petrographic variability of the samples.

Callcott *et al.* (1960) have established the following tentative relationships between Gray-King coke type and behavior in industrial ovens:

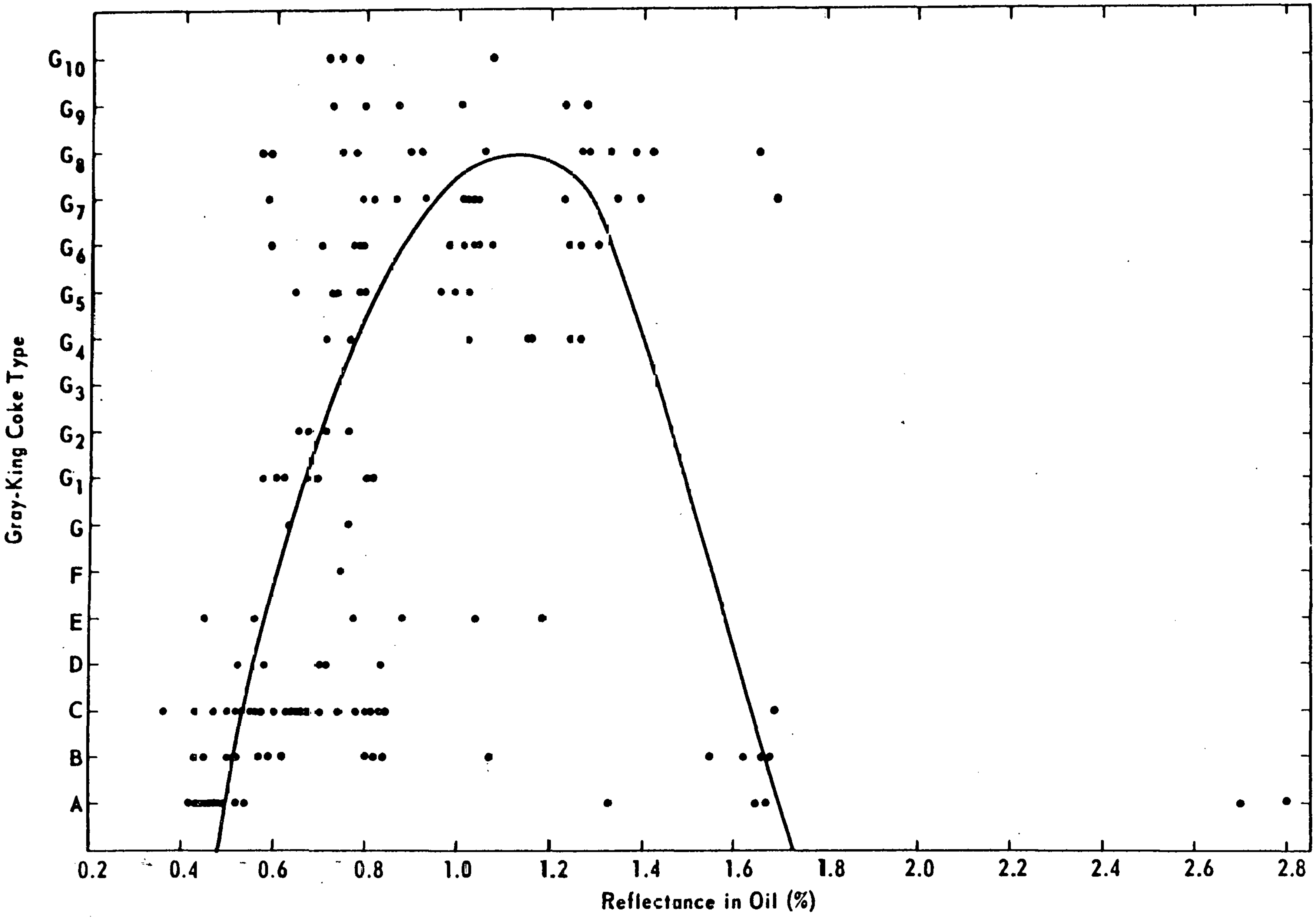

Figure 16. VARIATION IN GRAY-KING COKE TYPE OF U.S. COALS WITH RANK (REFLECTANCE)

Gray-King Coke Type	Industrial Coke Quality
A - C	Non-coking
D - F	Non-coking to very poor
G - G_3	Poor to fair cokes
G_4-	Good to excellent cokes

The Gray-King coke test is only rarely performed in the United States. However, like the free swelling index test, it is an alternative parameter for classifying coals by the current International classification system (United Nations Economic Commission for Europe, 1956). For this reason the Coal Research Section of The Pennsylvania State University routinely performs this test on all of the coal samples which it characterizes.

C. Plastometers

The essential criterion of a coking coal is its ability to soften, remain plastic through a range of temperature, and resolidify to form a strong, compact coke. To evaluate this set of characteristics, various plastometers have been developed. These show the resistance to movement offered by powdered coal when it is heated at standard heating rates. The two principal types of plastometer are:

1. the constant-torque plastometer, in which the torque applied to a stirring mechanism is held constant and the rate of movement of that mechanism is noted as a function of temperature.
2. The variable-torque plastometer, in which the stirring unit is rotated at constant speed and the opposing torque is measured.

The Gieseler Plastometer is the most commonly used contant-torque plastometer; variable-torque plastometers include the Brabender and the Cerchar.

The ASTM (1976c) version of the Gieseler test is performed on minus 40 mesh coal. A stirrer fitted with rabble arms is compacted into the coal packed in a cylindrical crucible. A constant torque of 40 g-in. is applied to the stirrer. As the coal softens when heated above 300°C at 3°/min, the torque causes the stirrer to move and the rate of movement is indicated by a pointer on a dial. Measurement can be visual or automatic.

The significant measurements are:

a) initial softening temperature, at which the dial movement reaches 1.0 dial divisions/minute (dd/min).

b) temperature of maximum fluidity, at which the dial reaches its maximum rate of movement.

c) solidification temperature at which the dial movement stops.

d) the maximum fluidity, which is the maximum movement expressed as dd/min.

The temperature range (c-a) is referred to as the fluid temperature range or plastic range. Fusion temperature, taken as that at 5 dd/min, is reported in some other systems of measurement.

Plastometer data are used as aids in blending coals for coke making. Ideally the fluid temperature ranges of blend components should overlap so that there is greater possibility of binding. Coals of high fluidity may be blended with coals of low fluidity to give far better cokes than can be achieved by coking either of these components individually. Laboratories of some U.S. steel companies routinely perform the Gieseler plastometer test to corroborate their evaluations of the coking potential of newly acquired coals and blends. In the Japanese steel industry, maximum fluidity has been used together with reflectance to monitor the composition of multicomponent coking blends.

There are already several indications that the potential for liquefaction of coals may be related to their plastic properties (Davis *et al.*, 1976); the tendency of certain coals to soften and swell at elevated temperatures could physically aid their hydrogenation and solvation, or under unfavorable conditions, lead to the irreversible production of inert coke.

The plastic properties of some bituminous coals can introduce problems in gasification processes, during which the fine coal particles fed into the reaction vessel tend to form agglomerated masses. One means of reducing the agglomerating capacity of coals is to subject them to a limited surface oxidation. The Gieseler plastometer has been demonstrated to be one of the most sensitive means of detecting coal oxidation, often recording loss of fluidity before any change can be observed in the chemical composition or the free swelling index. Oxidation usually causes a rise in softening temperature and smaller decrease in the resolidification temperature, so that the total effect is a reduction in the plastic range. Lower ranks of coal tend to oxidize more readily (Loison *et al.*, 1963).

The Gieseler test does not provide absolute measurement of fluidity because of the nature of the equipment and the fact that the measurements are being taken on a system in which fluid, solids and gases are mixed and interacting. Significant differences have been found among the results obtained from different designs of the Gieseler apparatus.

D. Dilatometers

Another means of measuring the plasticity of coal uses the contraction and expansion which occur during heating. Several types of equipment are employed for this purpose, although the two instruments in most common use are the Audibert-Arnu and Ruhr dilatometers.

In the Audibert-Arnu dilatometer a molded pencil-like cylinder of coal is heated from 300°C at 3°/min; movement of a piston which rests on the pencil is recorded on a scale or drum by means of a pointer or pen. The percentages of contraction and expansion are read directly or calculated.

Like the plastometer, the dilatometer is often employed as a means of assessing the potential of coals for carbonization, and the detection of the extent of oxidation. Dilatation as measured in the Ruhr dilatometer is one of the parameters in a coal classification system which recently has been proposed (Marshall, 1976)..

VIII. HARDNESS AND GRINDABILITY

A. Vickers Microhardness

The Vickers microhardness test is one which measures hardness as a function of the depth of penetration of a loaded diamond point (see van Krevelen, 1953; Honda and Sanada, 1956).

Values have been obtained from 248 U.S. coal samples using a Leitz Miniload tester equipped with a Vickers indenter. Because the readings were taken on vitrain bands, they are independent of petrographic composition, unlike the Hardgrove grindability which is influenced considerably by this factor. Measurements were made on plane surfaces prepared using standard polishing techniques. The rank parameter used in Figure 17 is maximum reflectance which also is independent of petrographic composition. The relationship between microhardness and rank, as shown by the plot of points in this figure corresponds with curves published by Honda and Sanada (*ibid.*) and van Krevelen (1961). Among points plotted according to their geological source, no striking segregation can be observed, although there is a suggestion of a population of coals from the Rocky Mountain province on the high microhardness side, and perhaps of a tendency for coals of the Western region of the Interior province to lie toward the lower side of the general trend of high volatile coals.

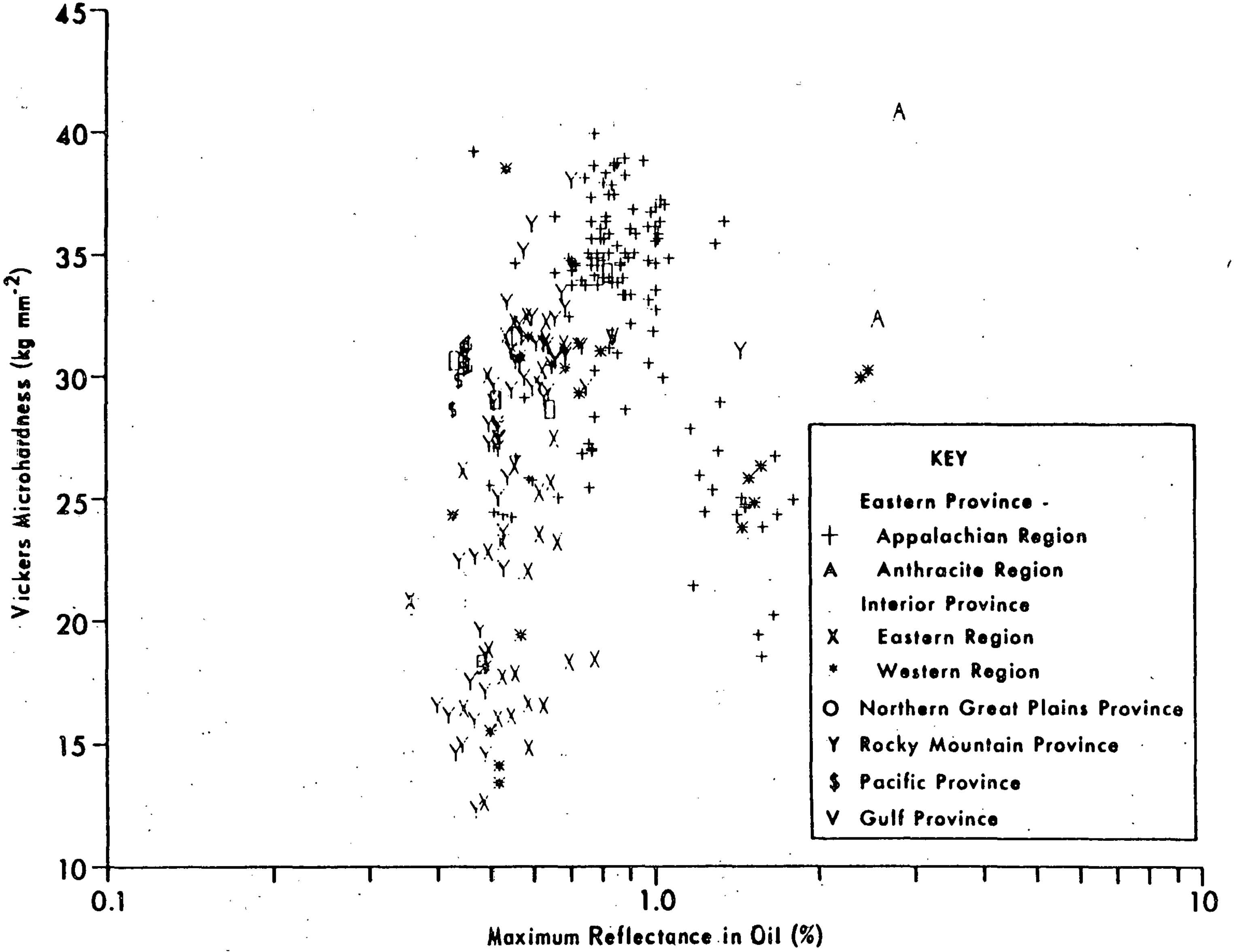

Figure 17. VARIATION IN VICKERS MICROHARDNESS OF U.S. COALS WITH RANK (REFLECTANCE)

B. Hardgrove Grindability Index

The test determines the relative ease of pulverization of 16 x 30 mesh coal samples in a standard pulverizer (ASTM, 1976a). The Hardgrove index has been measured routinely for 302 samples which have been collected in the course of a coal characterization program at The Pennsylvania State University. Coals from each of eight coal provinces and regions are represented in Figure 18, as in Figure 17, by different symbols. In this plot of grindability versus rank, it is apparent that there are distinct populations that tend to represent the geographic source areas. Note, for example, the grouping of anthracites from Pennsylvania. The general pattern of increasing grindability with decreasing rank to a maximum at a reflectance of 1.6 percent (approximately equivalent to a volatile matter (daf) of 20 percent) is in agreement with the results of other workers as compiled by Brown and Hiorns (1963). These authors also noted that the grindabilities of lignites from the southern states lie on the high side of the general trend for foreign coals. The present results support such an observation, and show that the lignites from the Northern Great Plains province have high grindabilities compared to the higher rank coals from the Rocky Mountain and Pacific provinces. Consequently, there appears to be a minimum for the grindability of American coals that lies within the range of 0.4 to 0.6 percent reflectance (or approximately 75 percent carbon). The effect of moisture on the grindability of lignites may account for some of the differences between the results reported previously and those given in this report. The lignites tested in this program were in an air-dried condition.

IX. SUMMARY AND CONCLUSIONS

Many of the tests used to characterize the physical properties of coal are empirical--often they do not represent adequately the process for which

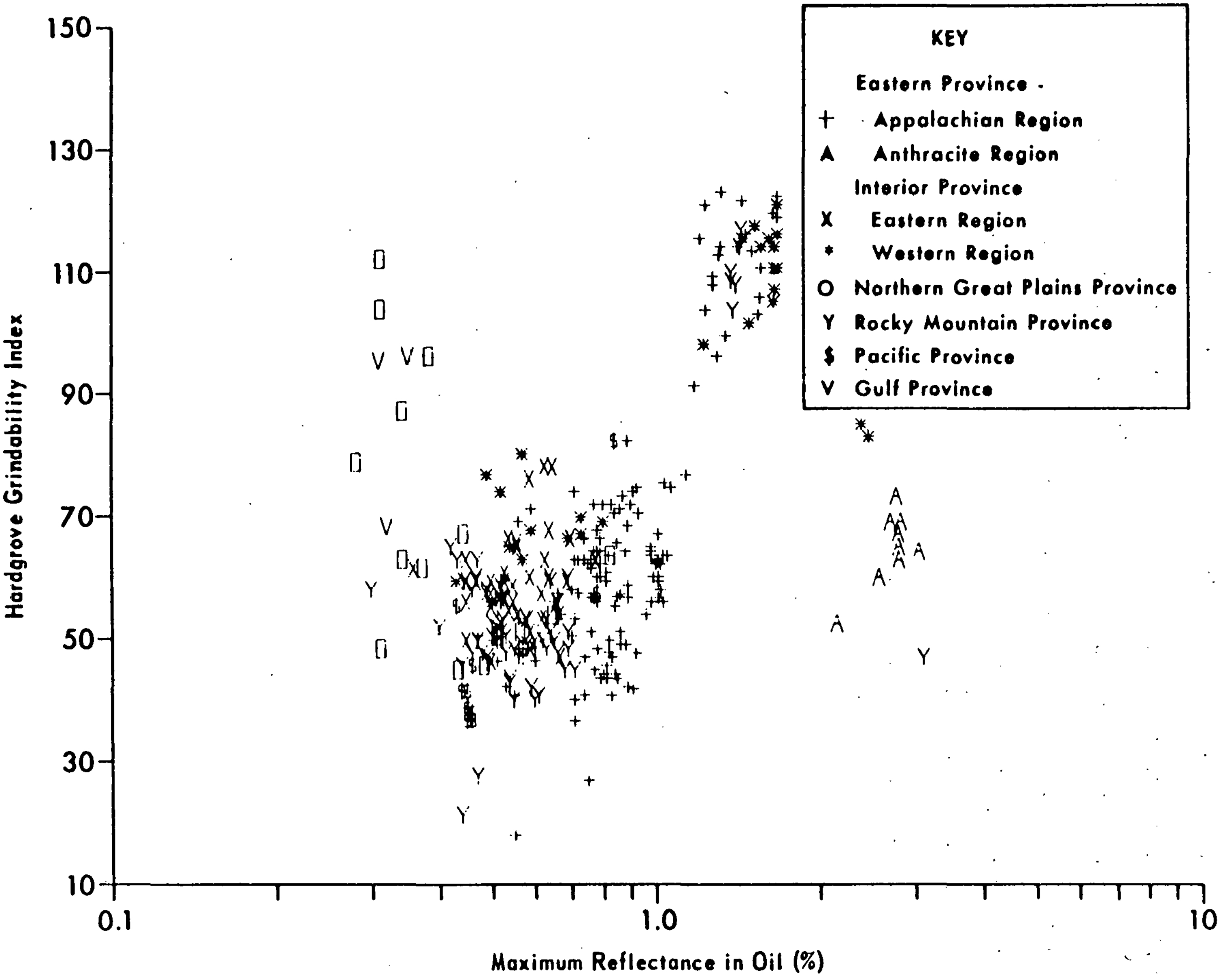

Figure 18. VARIATION IN HARDGROVE GRINDABILITY INDEX OF U.S. COALS WITH RANK (REFLECTANCE)

they are supposed to provide characterization. Results can be influenced by conditions of moisture, temperature, petrographic heterogeneity, and the concentration of flaws such as bedding or cleat. Direct measurements of several of the physical constants of coals have been made, but rarely have they been accepted as methods for routine characterization.

The present energy situation has provided the challenge and perhaps the opportunity to update, extend and improve our knowledge in the area of basic coal science in order to support the developments in coal technology which will be needed in the next decades.

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