

Data evaluation of trace elements determined in Nigerian coal using cluster procedures

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Abstract

Large data-sets of elements determined by instrumental neutron activation analysis (INAA) require meaningful interpretation in order to determine the pattern of their existence in host matrices. This could be achieved using cluster procedures. Element abundances (Al, As, Ba, Br, Ca, Ce, Cs, Dy, Eu, Fe, Ga, Gd, Hf, K, La, Lu, Mg, Mn, Na, O, Rb, Sb, Sc, Sm, Sr, Ta, Tb, Th, Ti, U, V, Yb, Zn and Zr) of prepared and run-of-mine coals from eight principal mines (Onyeama, Ogbete, Enugu, Gombe, Asaba-Ugwashi, Okaba, Afikpo and Lafia) in Nigeria were determined by INAA. Quality control of the measurements was assured by the re-determination of a standard reference material, NIST 1632a. These data-sets were then tested for multi-variate statistics using METHOD = SINGLE in the cluster procedure. The computer-assisted package SAS was used to generate the dendrograms while the algorithm used was stored Euclidean distances. The results showed a recognition pattern, useful for the interpretation of coalification histories and the prediction of fuel ranking for Nigerian coals. High segregation of coal fly ash was observed, while metallurgical coal grouped together with high-ranking coals of Okaba, Enugu and Obi (Lafia). Further work revealed some of these coals as having high gross calorific value (7908 kcal kg⁻¹ for Enugu coal; 7200 kcal kg⁻¹ for Okaba) and low sulphur thereby making them efficient fuel materials.

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1. Introduction

Cluster programs produce a pattern that allow for a more resolved visualization of the similarities existing between objects (e.g. coal samples from different sources) as related to some determined variables (i.e. elemental concentrations) especially when the latter is very large. This is achieved through a reduction of the n -dimensional determined space in which the samples exists as points, to a plane, permitting increased readability, pattern recognition and size reduction of the classifying parameters investigated (Buckner and Lotz, 1989; Hopke et al., 1987; Op de Beck, 1984). Cluster

analysis is most useful where most statistical methods cannot satisfactorily interpret existing trends in spatially heterogeneous multi-elemental concentrations associated with sedimentary environments of the earth's crust (Ewa et al., 1992; Ogugbuaja, 1978; Webster, 1978) as is usually the case with geochemical data.

Data evaluation of element concentrations of Nigerian coal samples was achieved using hierarchical clustering methods. This formation allows a cluster to be within another cluster but not overlapping with other clusters (Massart and Kaufman, 1983; Wong, 1982). Cluster methods based on hierarchical procedures begin by taking each observation as a cluster itself followed by the merging of the two closest to form a new cluster thereby replacing the two old clusters. Merging of two closest clusters is then repeated until only one cluster is left at the final stage. Hierarchical clustering therefore

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completes $(n - 1)$ fusion steps starting from n clusters, with each step being assigned a similarity coefficient.

The objective of this cluster analysis was aimed at investigating existing similarities for different types of coals mined in Nigeria based on the concentration of trace elements in each coal. This could be useful in assessing a priori coal ranking and also the extent of environmental contamination emitted by each coal due to enrichment after combustion. The statistical result so obtained could be used as a quick-guide in isolating low-ranking coals from the others thereby minimizing expenses on the mining of several coals that may not be relatively useful with respect to others, as energy sources.

2. Experimental

2.1. Sample preparation

As-received coal samples from the Nigerian Coal Corporation Enugu were obtained for instrumental neutron activation analysis. The coals were categorized into three classes. The first class consist of run-of-mine coals from Nigeria’s principal coal mines of Gombe, Ogbete, Onyeama, Azagba, Afikpo, Lafia(Obi), Enugu (Ekulu) and Okaba. The second class includes prepared coals (coal Briquettes, coke-char, formed coke, washed coal, metallurgical coke, lignite), which have all been modified in the laboratory through various stages of beneficiation and cleaning. Thirdly, coal by-product (Fly Ash) obtained through combustion was also used for the

study. The sample identification codes as depicted on the dendrogram (Fig. 1) are shown in Table 1.

Pulverization of the as-received samples was performed using crushers, agate-mortar and pestle. The pulverized samples were poured into heat resisting pyrex beakers and heated for 20 h at a temperature of about 106–110°C under specifications as stated by the American Society for Testing and Materials (ASTM) Committee D-5, responsible for the developments of methods of sampling, analysis and testing of coke and coal (Montgomery, 1977).

Table 1
Sample identification codes

Sample reference	Sample description
CT1	Briquette from carbonized coal
CT2	Coke char
CT3	Formed coke
CT4	Onyeama coal
CT5	Enugu washed coal (50–200 mm)
CT6	Enugu washed coal (20–50 mm)
CT7	Enugu washed coal (0–20 mm)
CT8	Ogbete coal
CT9	Enugu coal (Ekulu Mines)
CT10	Metallurgical coke
CT11	Gombe coal
CT12	Azagba-Ugwashi lignite
CT13	Okaba coal
CT 14	Afikpo coal
CT 15	Fly Ash (Enugu coal)
CT 16	Lafia (Obi) coal

Source: Nigerian Coal Corporation, Enugu.

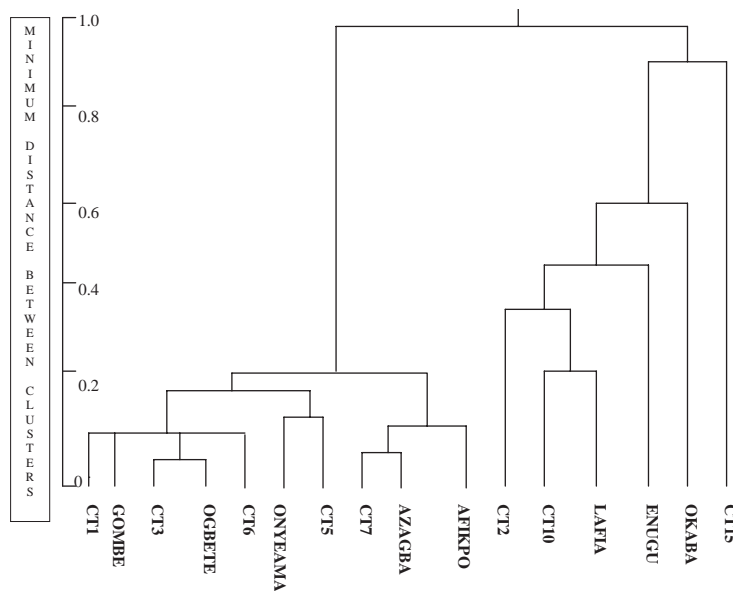


Fig. 1. Dendrogram showing the clusters of all the Nigerian coals investigated.

About 50–70 mg of the dried samples was then transferred into dry pre-labeled 2/5-dram polyethylene vials. The vials were heat-sealed and packed in a rack ready for transfer into aluminum cans for irradiation. Both the multi-element comparator NIST 1633a and the quality control standard NIST 1632a used for instrumental neutron activation analysis (INAA) were prepared in a similar manner, as described above, for the samples.

The samples for fast neutron activation analysis (FNAA) were encapsulated in relatively larger vials ($3.2 \times 1.4 \text{ cm}^2$). These vials were again loaded into 2-dram polyethylene vials acting as ‘rabbits’ for the pneumatic transfer system. The relatively large space available for samples allow sufficient volume of most material to be exposed to the neutrons at irradiation position thus optimizing sensitivity.

The choice of the 2-dram transfer vial is determined by the dimensions of the inner diameter of the pneumatic transfer tube of the 14-MeV Neutron Generator of Texas A and M University. The leftover volume in the 2-dram vial was filled up with melted paraffin. As the paraffin finally cools down inside the 2-dram vials it provides an accurate spacer, which does not allow geometrical displacement of the 2/5 dram vials within the 2-dram containers during impact at rapid transfer pressures between loading desks and irradiation positions.

2.2. Irradiations

Two facilities were used for the irradiation viz.

- (a) 1 MW Triga Mark I Swimming Pool-Type, research reactor of the Nuclear Science Centre of Texas A & M University, and the
- (b) 14 MeV A710-Kaman Science Neutron Generator of the Centre for Chemical Characterization and Analysis, Texas A & M University.

Samples and standards were irradiated using the pneumatic transfer system (short irradiations) and a rotisserie system (long irradiations) that uses in-core receivers having facilities that rotate samples during irradiations in the reactor. The irradiation procedures adopted are discussed below.

2.2.1. Pneumatic-tube irradiations

The P-tube irradiations of both standards and samples were performed at reactor core location C-2 where the flux determined was $1.0 \times 10^{13} \text{ n cm}^{-2} \text{ s}^{-1}$ with a thermal to epithermal neutron ratio (f -value) being in the range of 115–120. Samples, standards, and quality controls were irradiated for 30 s and cooled for 15 min before they were counted.

2.2.2. Rotisserie irradiations

In order to expose all the samples to a fairly homogenous neutron flux all through during the 14-h continuous long irradiation, the rotisserie (rotating) mode was employed. Aluminum cans with a capacity of twelve 2/5-dram vials were used in loading the samples, standards, quality controls, and blanks. Six of these cans were stacked and loaded into a rotisserie tube for irradiation at reactor core location A-6 where the neutron flux as monitored through the use of gold foils was $9.0 \times 10^{13} \text{ n cm}^{-2} \text{ s}^{-1}$.

2.2.3. Fast neutron irradiations

This irradiation was necessary for the determination of oxygen in the coal samples through the $^{16}\text{O}(n, p)^{16}\text{N}$ reaction and which could not be measured by the use of thermal neutrons via the (n, γ) reaction.

2.3. Gamma-ray spectroscopy

Different detectors and data acquisition systems were used during the analysis. Short-lived radionuclides were detected using a Ge(Li) detector (Canberra Industries Inc., Meriden, CT). This detector has a resolution of 1.8 keV full-width at half-maximum (FWHM), for Co-60 source at 1332 keV and an efficiency of 16%.

The intermediate-lived radionuclides were determined at another station using a Ge detector (Canberra Industries Inc., CT, Model 7229) with an efficiency of 18% and a resolution of 1.79 keV.

For the long-lived radionuclides a third station was used with a Ge–Li detector (EG and G Ortec Model Gem-22170-S, Oak Ridge, TN) having a resolution of 1.68 keV for Co-60 at the 1332 keV peak energy. The efficiency of this system was 22%.

A Westphall loss-free counting (LFC) system model ND 581 was used for the improvement of the counting statistics thus compensating dead-time losses. Detailed descriptions of the counting schemes used in this analysis are given in Table 2.

3. Cluster analysis

Input data (the rare earth element concentrations) determined for all the coals (run-of-mine coals, prepared-coals and coal fly-ash a coal by-product) were subjected to cluster analysis using the statistical analysis system (SAS) computer software. SAS programs of the Computing Services Centre of Texas A and M University were used in studying the clustering pattern of the coal samples. Hierarchical clustering was achieved using PROC CLUSTER while the Method chosen is the SINGLE LINKAGE (SAS, 1985). This method determines the similarity coefficients in the clustering as a measure of the minimum distance between clusters.

Table 2
Counting scheme for the elements analyzed from Nigerian coals

Schedule	Irradiation time	Cooling period	Counting interval	Elements detected
Short-lived	30 s	15 min	500 s	Al, Ba, Dy, Mg, Mn, Ti, V
Intermediate I	14 h	6 days	20 min	As, Br, Ca, K, La, Na, Sm
Intermediate II	14 h	10 days	20 min	Lu, U
Long-lived	14 h	26 days	1 h	Ce, Cs, Eu, Gd, Hf, Fe Rb, Sb, Sc, Sr, Ta, Tb, Th, Yb, Zn, Zr.

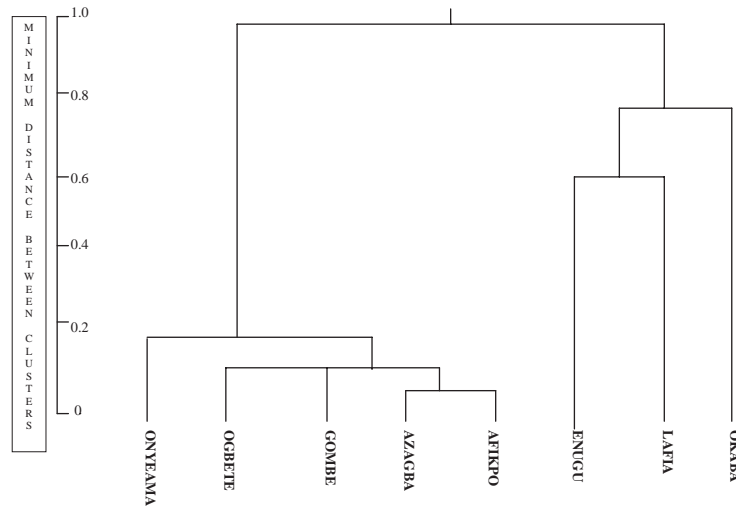


Fig. 2. Dendrogram of cluster output for only run-of-mine coals investigated with three high-ranking coals (Okaba, Lafia and Enugu) segregating from others.

Single Linkage has many theoretical properties exploited for cluster studies (Jardine and Sibson, 1971; Fisher and Van Ness, 1971; Hartigan, 1981). The METHOD = SINGLE LINKAGE was chosen for this work as a result of the fact that emphasis was needed to show how similar the data obtained from each coal deposit could relate to another closely related one regarded in clustering technique as ‘nearest-neighbours’. The dendrograms obtained through cluster analysis of coal data, using the SINGLE LINKAGE method is shown in Figs. 1 and 2.

4. Results and discussion

The range for each element determined from the fresh run-of-mine coals are given in Table 3 while the quality control results for the analysis using the reference material NIST 1632a is given in Table 4.

Data evaluation resulting in specifying SINGLE = METHOD in the cluster procedure yielded two dendrograms (Figs. 1 and 2) as outputs for all the coals analyzed. Fig. 1 shows a clustering of both run-of-mine

coals as well as laboratory prepared coals. The interpretation of the dendrograms is as follows.

Two major clusters could be seen from Fig. 1. At a dissimilarity coefficient of less than 0.2, ten coals (CT1, Gombe, CT3, Ogbete, CT6, Onyema, CT5, CT7, Azagba, Afikpo) clustered to form one group. Seven coals (CT2, CT10, Lafia, Enugu, Okaba and CT15) formed a second group covering a dissimilarity of about 0.1 upwards and close to 1.0. One success in the result of this clustering procedure is that coal CT15 remained an outlier from other groups, standing out alone. This was a convincing evidence of the success in the cluster analysis since coal codes in Table 1 reveals that this sample is actually fly ash which is a coal by-product of combustion from Enugu coal coded Enugu coal fly ash in Table 1. The elemental composition of fly ash is not similar to that of fresh coals hence the segregation as an outlier.

Outliers show disproportionate effect in multivariate analysis and do not tend to cluster at some levels with their sub-groups (Yarzab et al., 1980). The input data also revealed that the concentrations of the elements determined for CT15 (Enugu Fly Ash) grossly differed

Table 3
Element abundances in Nigerian coal as they compare with other coals (concentrations are given in ppm or in % as specified)

Element	Nigeria (this work)	USA (Torrey, 1978)	China (Chen et al., 1986)	World-wide average (Valkovic, 1983)
Al (%)	0.39–8.86	0.43–3.04	NA	1.0
As	0.19–9.10	0.5–106	0.32–120	5.0
Ba	334.26–719.10	NA	12.8–1540	500
Br	0.96–6.48	4.0–52.0	0.12–46.9	NA
Ca (%)	0.07–0.96	0.05–2.67	NA	1.0
Ce	3.57–90.31	NA	3.43–183	11.5
Cs	0.41–112.47	NA	0.0067–33	NA
Dy	0.90–6.41	NA	NA	NA
Eu	0.13–1.99	NA	0.021–2.0	0.7
Fe (%)	0.15–2.13	0.32–4.32	2.0–4.5	1.0
Gd	0.71–10.20	NA	NA	1.6
Hf	0.58–16.19	NA	0.31–15.9	NA
K (%)	0.001–0.54	0.02–0.43	0.01–1.3	0.01
La	1.31–29.02	0–98	0.58–91.6	10
Lu	0.03–0.48	NA	0.014–1.04	0.07
Mg (%)	0.02–0.27	0.10–0.25	NA	0.02
Mn	15.0–288.33	6–181	NA	50
Na (%)	0.04–0.04	0–0.2	0.002–4.6	0.02
O	17.96–49.90	NA	NA	NA
Rb	0.75–33.5	NA	1.4–93.8	100
Sb	0.68–13.38	0.2–9.0	0.047–28.6	3.0
Sc	0.75–12.37	10–100	0.12–18.3	5
Sm	0.52–7.19	NA	0.08–14.4	1.6
Sr	15.49–402.77	NA	27.4–894	500
Ta	0.14–2.16	NA	0.067–4.5	NA
Tb	0.02–0.97	NA	0.07–2.1	NA
Th	1.10–15.5	NA	0.09–25.4	NA
Ti (%)	0.05–0.92	0.002–0.32	NA	25
U	0.39–7.27	10–100	0.16–21	1.0
V	3.55–113.9	0.1281	NA	25
Yb	0.24–73.71	NA	0.406–6.19	0.5
Zn	0.66–73.71	0–0.56	0.56–192	50
Zr	6.38–1615	8–133	NA	NA

from Enugu coal itself. This itself proved how successful cluster methods could be in segregating data which are dissimilar as shown in this study. Three run-of-mine coals clustered together namely: Lafia, Enugu and Okaba. These coals are sub-bituminous coals; relatively higher in coal ranking than others. Another set of three coals of interest also grouped together (CT2, CT10, Lafia). From the sample codes, CT2 is Coke char while CT10 is Metallurgical Coal. These are all coking coals and are usually in high demand for iron smelting processes in Steel Complexes such as the Ajaokuta Steel Complex in Nigeria. It is well known that the Lafia (Obi) deposit holds a total reserve of 22 million tonnes of coking coal (FMPMR, 1993). It is not surprising therefore, that Lafia coal clustered in the same subgroup as coal CT2 (Coke Char) and CT10 (Metallurgical Coke).

An attempt was made to re-investigate the clustering tendencies (Fig. 2) of only fresh coals obtained from the

different mines in Nigeria. Again two classes emerged. The three high-ranking sub-bituminous coals (Enugu, Lafia, Okaba) clustered together, persistently, while the other coals (Onyeama, Ogbete, Gombe, Azagba, Afikpo) remained in another group. From this segregation, it becomes very obvious that the other coals have quite different characteristics.

Further work on these coals was performed by assessing the oxygen levels of the fresh coals, using the 14 MeV neutron activation analysis. From Table 5 it could be seen that three coals (Enugu, Okaba, and Lafia) have higher oxygen levels than the other coals. It is well known that oxygen levels determine the degree of coal combustion, combustion-reactivity and rank properties (Hensel, 1979).

Further investigation into other sources of data revealed that the Enugu and Okaba coal are well documented and have been investigated upon by the Nigerian Coal Corporation (Table 6). Thus cluster

Table 4
Determination of elemental abundances of NIST 1632a as quality measurements for the analysis (concentrations are given in ppm or in % as stated)

Element	Consensus values (Gladney et al., 1987) Mean \pm SD	This work ($n = 4$) Mean \pm SD
Al (%)	2.95 \pm 0.10	3.16
As	9.2 \pm 0.5	8.84 \pm 0.49
Ba	120 \pm 15	131.31 \pm 36.5
Br	41 \pm 2	43.78 \pm 8.48
Ca (%)	0.24 \pm 0.01	0.25 \pm 0.04
Ce	29 \pm 2	30.41 \pm 2.29
Cs	2.3 \pm 0.2	2.46 \pm 0.09
Dy	2.06 \pm 0.14	2.05
Eu	0.52 \pm 0.04	0.56 \pm 0.03
Fe (%)	1.11 \pm 0.03	1.12 \pm 0.04
Gd	2.6 \pm 0.6	3.01 \pm 0.24
Hf	1.62 \pm 0.15	1.63 \pm 0.04
K (%)	0.41 \pm 0.02	0.43 \pm 0.09
La	15 \pm 2	13.61 \pm 0.34
Lu	0.17 \pm 0.02	0.17 \pm 0.02
Mg (%)	0.12 \pm 0.02	0.10 \pm 0.01
Mn	27.2 \pm 1.4	30.72 \pm 3.46
Na (%)	0.082 \pm 0.007	0.080
Rb	30 \pm 2	29.61 \pm 2.53
Sb	0.6 \pm 0.045	0.63 \pm 0.13
Sc	6.3 \pm 0.3	6.23 \pm 0.36
Sm	2.4 \pm 0.3	2.51 \pm 0.02
Sr	85 \pm 6	99.85 \pm 25.87
Ta	0.42 \pm 0.04	0.47 \pm 0.05
Tb	0.311 \pm 0.013	0.313 \pm 0.068
Th	4.5 \pm 0.2	4.66 \pm 0.26
Ti (%)	0.163 \pm 0.013	0.175
V	44 \pm 2	47.67 \pm 1.3
Yb	1.09 \pm 0.09	1.15 \pm 0.09
Zn	27.2 \pm 1.4	30.72 \pm 3.46
Zr	53 \pm 5	55.85 \pm 2.54

Table 5
Oxygen levels in Nigerian coals as determined by 14 MeV neutron activation analysis

Coal samples (deposits)	Mean (SD) ($n = 21$)
Enugu	31.68 (0.78)
Okaba	49.90 (5.15)
Lafia	31.32 (1.60)
Gombe	28.33 (0.32)
Onyeama	17.96 (0.53)
Afikpo	25.47 (0.87)
Azagba	25.57 (0.74)

analysis of the elemental concentrations of all the coals analysed confirms that certain coals have close similarities and are dissimilar to others based on their element compositions.

Table 6
Fuel properties of Enugu and Okaba coals

Properties	Enugu coal	Okaba coal
<i>Proximate analysis (wt%)</i>		
Ash	10.3	11
Volatile matter	44.8	46
Coke	54.6	55
<i>Ultimate analysis (wt%-dry ash free)</i>		
Carbon	79.4	78
Hydrogen	5.2	6
Sulphur (total)	0.75	1
<i>Gross calorific value</i>		
MJ/kg	33	30.3
kcal/kg	7908	7200
<i>Fischer assay</i>		
Free swelling index	1	0.5
<i>Dilatometric properties</i>		
Softening point ($^{\circ}$ C)	36	380
Contraction (%)	27	18

Source: Nigerian Coal Corporation, Enugu.

5. Conclusion

Cluster techniques have been successfully used in presenting a rapid visualization of the diversity in the grouping of Nigerian coals. The following conclusions were drawn from this work:

- (i) The stability of the clustering has been tested and confirmed by two dendrograms (Figs. 1 and 2) depicting two major groupings. Cluster stability by exclusion of outliers and other data confirms the effectiveness of the technique and should be used as a basis for re-affirming group consistency (Everitt, 1977; Van der Sloot, 1980).
- (ii) Enugu, Lafia and Okaba coals persistently remained in the same group. This could suggest that they are likely related in elemental composition, exhibiting the same trend or that their coalification process may be comparable having undergone similar metamorphism. Data compiled in Table 6 as submitted by the Nigerian Coal Corporation has confirmed the similarity between Enugu and Okaba coals. There could be a strong relevance therefore in their geochemical evolution. If their trace contaminants lie within the same range, it could be inferred that the environmental problems therefore, associated with the combustion of these coals may not show wide departures from each other.

Broadly classifying Nigerian coals as low ranking may be insufficient to differentiate between them, as these coals tend to segregate when clustered. Ranking is used as a basis of coal classification with the sole aim of exploring coking properties. This model has since been considered inadequate by workers in coal technology (Given, 1960; Waddel et al., 1978; Yarzab et al., 1980; Van der Sloot, 1980). Cluster Techniques could be regarded as a novel basis and supplement for coal classification as suggested by these authors.

Finally, clustering of Nigerian coals showed that coals known to have been formed from the same geological formation (Onyeama, Enugu, Ogbete, Afikpo) need not have same elemental composition for them to remain in the same cluster. This suggests possible failure of band development in explaining coalification at the Benue-Trough. Although the Benue-Geosynclines (Benkhelil, 1982) must have given rise to coal mineralization in Nigeria, coal metamorphism does not leave coal bands and seams with identical coal element characteristics. This is attributed to the fact that diagenesis, late metamorphism and crustal tectonic forces that lead to the folding of the geosynclines could be localized leading to diversity as is clearly illustrated by the composition of Enugu, Onyeama and Ogbete coals derived from the same geological formation. Yarzab et al. (1980) confirmed the failure of band metamorphism from his study of Pennsylvanian coals formed during the mineralization of the Appalachian Geosynclines.

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References

Benkhelil, J., 1982. Benue trough and Benue chain. *Geol. Mag.* 119, 155–168.

- Buckner, G., Lotz, T., 1989. Using SAS/GRAPH software to create enhanced dendrograms. SAS Users Group International Conference Proceedings, SUGL 14, 14th Annual Conference, San Francisco, CA, USA, April 9–12.
- Chen, B.R., Qian, Q.F., Yang, Y.N., Yang, S.J., 1986. Proceedings of the Seventh International Conference on MTAA, Copenhagen, pp. 1169–1174.
- Everitt, B.S., 1977. *Cluster Analysis* 2nd Edition. Heineman Educational Books Ltd., London.
- Ewa, I.O.B., Oladipo, O.A., Dim, L.A., 1992. Cluster analysis of elemental concentrations of cored Nigerian river sediments. *J. Environ. Sci. Health. Environ. Sci. Eng.* 27 (1), 1–11 (Part A).
- Fisher, L., Van Ness, J.W., 1971. Admissible clustering procedure. *Biometrika* 58, 91–104.
- Federal Ministry of Petroleum and Mineral Resources (FMPMR), 1993. *Inventory of Nigerian Minerals, Mines and Miners*, Vol. 9. Mines Department, Lagos, Nigeria.
- Given, P.H., 1960. *Fuel* 39, 147.
- Gladney, E.S., O'Malley, B.T., Roelandts, I., Gills, T.E., 1987. *Standard Reference Materials; Compilation of Elemental Concentration Data for NBS Clinical, Biological, Geological and Environmental Standard Reference Materials*. US Department of Commerce.
- Hartigan, J.A., 1981. Consistency of single linkage for high density clusters. *J. Am. Stat. Assoc.* 76, 388–394.
- Hensel, R.P., 1979. Western Coals; Properties that Influence Boiler Design. In: *Coal Technology*, Vol. 2. Houston, TX, pp. 6–8.
- Hopke, P.K., Martin, R.C., Evins, M.A., 1987. The interpretation of multielemental INAA data using pattern recognition methods. *J. Radioanal. Nucl. Chem.* 112 (1), 215–222.
- Jardine, N., Sibson, R., 1971. *Mathematical Taxonomy*. Wiley, New York.
- Massart, D.L., Kaufman, L., 1983. *The Interpretation of Analytical Chemical Data by the Use of Cluster Analysis*. Wiley, New York.
- Montgomery, W.J., 1977. *ASTM Approach to the Standardization of New Techniques for Coal Analysis*, Vol. 22. American Chemical Society, Division of Fuel Chemistry, in preparation.
- Ogugbuaja, V.O., 1978. Statistical analysis of heavy metal concentrations from lake sediments. *J. Environ. Sci. Health Part-A Environ. Sci. Eng.* 20 (5), 529–554.
- Op de Beck, J., 1984. Clustering of samples and elements, based on multi-variable chemical data. Proceedings of the Fifth International Conference on Nuclear Methods in Environmental Energy Research, University of Missouri, Columbia, USA.
- SAS, 1985. *The CLUSTER Procedure, SAS User's Guide; Statistics Version, 5th Edition*. SAS Institute Inc., Cary, NC, pp. 255–315.
- Torrey, S., 1978. *Trace Contaminants from Coal*. Noyes Data Corp., New Jersey.
- Valkovic, V., 1983. *Trace Elements in Coal I and II*. CRC Press, Boca Baton, FL, pp. 130–150.
- Van der Sloot, H.A., 1980. Classification of coal by trace analysis using INAA, cluster analysis and leaching of precipitator ash. Proceedings of the Fourth International Conference on Nuclear Methods in Environmental and Energy Research, University of Missouri, Columbia, USA.

- Waddel, C.D.A., Spackman, W., Griffiths, J.C., 1978. Study of the interrelationships among chemical and petrographic variables of United States coals. Coal Research Section, Pennsylvania State University, Technical Report 9 to US Department of Energy, Report FE 2030-TR9.
- Webster, R., 1978. Optimally partitioning of soil transects. *J. Soil Sci.* 29, 388–402.
- Wong, M.A., 1982. A hybrid clustering method for identifying high density clusters. *J. Am. Stat. Assoc.* 77, 841–847.
- Yarab, R.F., Given, P.H., Spackman, W., Davis, A., 1980. *Fuel* 59, 81–90.