The Effects of Pyrite Grain Clustering on the Measurement of Total Sulfur

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ABSTRACT

The value _sulfur content in weight percent of a rock unit is extensively used to identify both the acid producing potential of coal associated rocks and the quality of coal. In the case of a coal associated rock, any underestimation in the value of sulfur content could lead to a misidentification of a potentially toxic rock material. An erroneously low estimate of the sulfur content of coal sample would result in the assignment of a higher quality of coal and s subsequent mis-utilization of the sampled coal.

Sulfur analysis of rock material is performed on a small. fractional (and assumed representative" portion of a larger sample. The small sample could be a sample taken from an outcrop or a sample of a rock unit exposed in a drill core. If the iron disulfide minerals in the rock stratum being analyzed are homogeneously distributed throughout the rock unit, the small sample will be representative of the rock unit. If, on the other hand, the iron ,disulfide minerals are not distributed throughout the rock unit, but rather exist for example, in isolated clusters of pyrite grains, then the small sample taken from the outcrop or from the drill core may NOT be representative of the entire rock unit-. In such a case the small sample will not exhibit the iron disulfide content characteristic- of the rock unit and certainly will not in any manner represent the mode in which the iron disulfides are distributed throughout rock unit. This obviously adds the element of chance to the accurate evaluation of the total sulfur content of the .sampled rock unit.

Through artificial intelligence it can be demonstrated that the degree to which the iron disulfide minerals in any particular rock unit are non -homogeneously distributed (existing in clusters rather than as discrete grains of equal dimensions uniformly dispersed throughout a rock unit) influences the analytical results. If the iron disulfide minerals are clustered then the analytical value of total sulfur content will be lower than the actual concentration. Assumptions made as to the uniform or homogeneous distribution of the iron disulfide minerals within a rock unit can be shown to be invalid. In addition the assumption that the total. sulfur contents determined for replicate samples of a rock unit exhibit a Gaussian or normal distribution can be shown to be invalid. The true distribution of for the total sulfur values of replicate analyses of a rock unit is better represented by a Poisson Distribution. A perfectly homogeneous iron disulfide distribution will, in fact, yield a normal distribution of analytical results that is simply an extreme case of a Poisson Distribution. The degree to which the iron disulfide minerals are non-homogeneously distributed in a rock unit can be

shown to control a single variable in the mathematical representation of a Poisson Distribution. This gives rise to a distribution of total sulfur analyses whose median is lower than the true total sulfur content for of the rock unit.

INTRODUCTION

The knowledge of three factors are critical to viable analytical conclusions relative to the abundance of any compositional parameter: 1) the mode of occurrence, 2) the sampling method, and 3) the distribution of replicate analytical results. In the analysis of rock materials, the first of these is rarely known. Information concerning the second and third factors either exists or can be generated. The interrelations that exist between these three parameters are illustrated in the following simple analog.

Consider the distributions of black squares shown in Figure 1 and Figure 2. The distribution of black squares for each board is 2 black squares per 10 total squares. However, the distribution pattern of the black squares is unique for each board. For this simplistic model , the manner of distribution of black squares for Figure 1- is 'uniform' (homogeneous) while 'clustered' non-homogeneous) for Figure 2. These scenarios represent the extremes of possible component distributions (homogeneous and non-homogeneous).

First, assume that the number of black squares are to be counted and the distribution (number of black squares per 10 total squares) of the black. squares is to be determined by BLINDLY throwing a dart at each board. There are 2 ways in which the black squares Can be so counted. First, the dart can be thrown at the board 10 times. The total number of black squares hit in 10 throws becomes the frequency of occurrence of black squares in 10. Second, a dart is thrown at the board. Not only is the square hit by the dart counted. but also the squares that are adjacent (up. down, left, and right) to the square hit with the dart. The total number of black squares hit per 10 total squares counted becomes the frequency of black squares in 10. Therefore, there are 2 Possible black square distributions (uniform and clustered) and two Possible counting Scenarios: (1) single or discrete throw counting and (2) adjacent square counting. The latter of these two sampling techniques is called a 'grab sample'.

The distribution of the results (black. squares per 10 total squares) for 10sampling events by each method yield different results. With respect to the DISCRETE THROW method of sampling there is little difference in the distribution of results (black squares per 10 total squares) between the UNIFORM and CLUSTER boards. ',see Figure 3 The GRAB method of sampling, however, produced a marked difference in the distribution of results. This can be seen in Figure 4 and Table 1. When the UNIFORM board is sampled by the (GRAB sampling method, the distribution of results are the same as the distribution of results for DISCRETE throw sampling shown in Figure 3. That is, if the black square distribution is uniform, both counting techniques give the same results. However, the combination of a CLUSTER board and GRAB sampling yield a distribution of results that are quite different from that gotten from the discrete throw method. The results can be seen in table 2.

TABLE 1. Black squares per 10 total squares using GRAB SAMPLING

trial	UNIFORM	CLUSTER
1	3	8
2	1	0
3	2	0
4	2	0
5	1	0
6	4	0
7	0	3
8	2	0
9	1	0
10	4	0

TABLE 2
NUMERICAL AVERAGES FOR 10 SAMPLING EVENTS

	SAMPLING SCENERIOS	
DISTRIBUTION SCENERIOS	DISCRETE THROW	GRAB SAMPLING
1. UNIFORM	2	2
2. CLUSTERED	2	1

The reason for this discrepancy of results is based in probability theory'. The method of 'discrete dart throws' is a by definition a 'Markov process'; one in which the present or n-th event (or outcome) is not controlled by the results of a previous (n-2)-th event. This is also referred to as a 'stochastic process'. Grab sampling, on the other hand, is not a Markov process in that the next square to be counted is determined by the square on which the dart fell (a previous or (n-2)th event). The reason that the distribution of results for the grab sampling method utilized on the UNIFORM board matched the Markov process is because the UNIFORM distribution of black squares on the uniform board compensated for the sampling method. The distribution of results seem more like a Markov process because the next square counted has 20% chance of being black. The true distribution is 2 black squares per 10 total squares. A visual examination of the Uniform board demonstrates that very few grab sampling events will fail to come up with at least a single black square. There is no such compensation when the CLUSTER board undergoes grab sampling. The next square counted has a high chance of being black if the dart landed on a black square. This is illustrated by the data in table 1 (i.e. the dart either found a bundle of black squares or none at all).

Another simple analogy deals with phone sampling. Two people are assigned to determine the number of people in the U.S. living in states beginning with the letter '0' based on 10000 telephone inquries. One decides to make 10000 telephone calls using random numbers to venerate a telephone number. The second sampler, in order to save money, decides to make 1000 telephone calls using random numbers to generate a telephone number. The sampler will ask the inquiree (samplee) to summon 10 of his or her neighbors to the phone so that the sampler can ascertain in which state they reside. Should this second sampler reach telephone numbers in Portland, Tulsa, or Cleveland a disproportionate number of times the final estimate could be too high. Conversely, should the sampler fail to reach Ohio, Oklahoma, or Oregon often, the final estimate could be too low. The result obtained by the first sampler is obviously better due to the fact that a Markov process was utilized in sampling a non uniform database.

DISCUSSION

The analyst charged with determining the content of a specific -component within a natural material is faced with the some of the *problems* cited *in these* simple analogies. Natural materials rarely exhibit compositional uniformity while at the same time, grab sampling is a basic sampling technique. A botanist seeking to determine the distribution of moth eggs within a large area must decide on a sub region of that area. When the first moth egg is encountered many more eggs can be expected to be in the same general vicinity. A geochemist faced with determining the total iron disulfide content in a rock unit faces the same dilemma. The geochemist is faced with determining the sulfur content of a rock unit must answer the following questions:

1. Is a rock sample taken from a particular portion of a rock unit representative of the entire rock unit for that area?
2. Is the distribution of sulfur in the sample of rock representative of sulfur distribution within the entire stratigraphic unit over the entire area?

In order to derive a definitive value for the concentrations of Sulfur in a rock unit, certain assumptions must be made. First, there is the assumption of homogenity. The value of total sulfur ,within a rock sample is obviously dependent on the concentration of iron disulfide minerals present in the rock. In practice a single sulfur analysis Performed on a single rock sample taken from a rock unit within a single drill core becomes an 'a priori' or accepted value of the total sulfur content for the entire layer of rock. For this to be true, the assumption that the iron disulfide minerals are homogeneously distributed within the unit must be valid. Only then can the result of the analysis be representative of the true sulfur content of the entire layer and have a 'high probability' of being correct. It is important to realize that there is no practical way In which the 'true' amount of iron disulfide minerals present in a cock unit can be determined without analyzing every last grain of the strata; obviously an impossible task. Unfortunately, the chemistry of the iron disulfide formation in anaerobic (swamp) paleoenvironments precludes any assumption of homogeneous distribution within any subsequently formed rock unit. Different sectors of these paleoenvironments will have had different microenvironments which will in turn contain different concentrations of iron and sulfate. different kinds of bacteria, and different kinds if animal or plant life. Within an environment exhibiting such (geochemical variability the production of a perfectly homogenous distribution of the iron disulfide minerals is highly improbable at best.

Iron disulfide grains are usually too small to be counted for any large volume of rock strata. However, in a study done by Stenstrom (1967) on siderite concretions (usually about 2-5-inches long) present in a shale in the Northeastern Illinois coalfields, he noted that [at a certain Peabody surface mine known as "Pit 11"] the distribution of these concretions ranged from 10 to 100 per cubic meter. The author noted that at the same site the siderite concretions were missing in some Darts and Plentiful in other parts. In addition, some clusters contain large numbers of siderite -concretions while in other clusters, the concretions are sparse. The same is true of the fossils contained within about 40% of these siderite concretions. Obviously, chemically different. anaerobic .conditions were Present in the paleoenvironments that produced both '.'-he large, visible siderite concretions and the small microscopic iron disulfide crystals.

In a study conducted by the authors, 108 rock samples from the northern West Virginia coal-fields were comprehensively examined with respect to mineralogy, acid production Parameters, and pyrite morphology (marcasite was relatively rare). These rock samples represent strata associated with the Upper Freeport, Lower Freeport, Upper Kittanning, Lower Kittanning, and Waynesburg coal beds. A Pyrite morphological study was conducted by Haines (1986) in which 46 of these rock samples of various lithologies were examined microscopically for 5 polymorphic forms of iron disulfide, including framboidal pyrite, massive pyrite, euhedral pyrite, isolated pyrite, and in a few samples marcasite. A statistical summary of the relative percentages and dimensions of each morphology for each lithology is shown in Table 3. The ranges for the Pyrite concentration values shown in Table _3 suggest a distribution scenario that is a combination of pyrite clustering -and pyrite homogenity. The small framboidal pyrite grains, for example, appear To be uniformly distributed, while the massive, euhedral, and isolated crystalline forms show clustering with a wide variance with respect to distribution (percentage) and size. Acid producing tests conducted on these samples revealed two interesting phenomena. First, in some samples more sulfate was leached from weathered samples than was possible based on the analytical total wt% sulfur analyses. This phenomenon occurred most frequently when the total wt% sulfur was low ($<$ 1%). Second, the molar ratio of ACID/SULFATE (ACID expressed as moles of hydrogen ion derived from acidity measurements) is rarely 2:1, which is the value assumed by the commonly used Acid-Base Account (Smith, 1978). (The numeric constant of 31.215- used by acid-base account to Predict the tons of calcium carbonate necessary to neutralize the acid generated by 1000 tons of material assumes a 2:1 ACID/SULFATE molar ratio.) A distribution histogram for the molar ratio (expressed as tons calcium carbonate per 1000 tons material per wt% total sulfur), obtained by 108 leaching experiments can be seen in Figure 5. The histogram is subdivided by coal bed. Note that the excessively high molar ratios (corresponding to a value greater than the factor of 31.25 used in the acid-base accounting procedure) occur only in lithologies associated with the Upper-Freeport and Lower Kittanning coal beds. There are two possible explanations for these observations: First, the chemical mechanisms responsible for the oxidation of iron disulfide minerals and subsequent acid production are more site specific than imagined. Secondly, the total wt% sulfur could have been underestimated by the analytical methodologies. More than "1-1/3 of the samples in this region 31.25)of the histogram in figure 5 had total wt% sulfur values less than 1%.

The microscopic morphological data reveal information which could serve to explain these observations. Figures 6 - 7 show that there 'are two morphological forms whose concentrations influence the total wt% sulfur 1) isolated crystals and 2) massive iron disulfide.

Isolated crystals are present in only small quantities when the total wt% sulfur is high. On the other hand the concentration of massive iron disulfide is directly related to the total wt% sulfur. (The euhedral and framboidal morphologies had no discernable trend with respect to total wt% sulfur.) Low values of total wt% sulfur is conspicuously void of massive iron disulfide in both size and amount as seen in Figure 8. The samples that produced more leachable sulfate *than was* stoichiometrically possible based upon the total - - sulfur analyses were all high in isolated crystals and low in qt % massive pyrite. Yet, some of these samples had excessively high ACID/SULFATE ratios. Two possible explanations exist: (1) Either the chemistry of the acid generation mechanism has changed or (2) a higher total wt% sulfur must be present than analytically indicated in order to agree with the accepted stoichiometry. The latter explanation seems more viable but at the same time carries with it the fact that the analytically determined total sulfur content must have underestimated the true sulfur content.

	ROCK TYPE				
	BONE COAL	SHALE PARTING	SEAT EARTH	ROOF SHALE	PREP REFUSE
wt % TOTAL SULFUR					
minimum percentage	1.46	0.94	0.19	0.80	2.74
average percentage	3.28	1.36	1.78	3.34	4.55
maximum percentage	5.26	4.24	3.81	5.26	6.33
FRAMBOIDAL PYRITE					
minimum percentage	3.00	4.00	2.00	1.00	1.00
average percentage	6.00	14.11	9.00	4.22	4.25
maximum percentage	10.00	25.00	20.00	11.00	10.00
minimum dimension	10.00	10.00	11.00	6.60	11.00
average dimension	13.00	15.11	25.00	9.56	12.75
maximum dimension	17.00	22.00	56.00	12.00	15.00
MASSIVE PYRITE					
minimum percentage	39.00	2.00	4.00	0.00	23.00
average percentage	45.00	12.67	16.00	38.00	45.00
maximum percentage	56.00	48.00	21.00	75.00	67.00
minimum dimension	67.00	9.1	44.00	188.00	220.00
average dimension	174.33	133.47	84.75	302.12	314.25
maximum dimension	250.00	218.00	103.00	445.00	390.00
ISOLATED CRYSTALS					
minimum percentage	18.00	28.00	43.00	7.00	27.00
average percentage	32.33	65.00	64.75	49.00	34.00
maximum percentage	46.00	93.00	90.00	99.00	51.00
minimum dimension	2.00	1.80	2.80	1.90	2.20
average dimension	2.13	2.02	2.13	2.20	2.20
maximum dimension	2.20	2.20	2.70	2.70	2.20
EUHEDRAL PYRITE					
minimum percentage	9.00	0.00	2.00	0.00	2.00
average percentage	12.67	8.22	10.25	6.89	4.00
maximum percentage	18.00	15.00	17.00	22.00	8.00
minimum dimension	18.00	3.00	14.00	4.40	6.60
average dimension	62.67	32.42	42.75	91.55	77.40
maximum dimension	150.00	87.00	98.00	263.00	220.00

The MACS Software

The problem that now faces the analyst is the level of confidence or reliance should be assigned to the value of a single sulfur analysis or to the basic assumption of homogenity of iron disulfide distribution since the 'true' value is unknown. The only way to ascertain the answer is to find a rock. unit for which both the amount of iron disulfide minerals present and the mode of distribution (clustered, homogeneously distributed, or some combination of both) of iron disulfide minerals are exactly known. This rock unit must then be analyzed numerous times, followed by statistical analysis of the distribution of analytical results.

Unfortunately, a 'real world' study of this kind is not feasible. This kind of study can, however, be Performed by using elements of artificial intelligence through computer simulation. A computer can be instructed to construct a large block of rock in units of cubic microns where the composition of each cubic micron is exactly known. The computer can then be given a set of instructions that will extract replicate samples from any portion of this block any number of times, and determine the pyrite (or sulfur) content of each sample extracted.

'The Mineralogical Analysis by Computer Simulation (MACS) software was developed to perform this task. MACS designs a large block of rock -and fills each cubic micron with any desired material. Pyrite (or any other mineral) can be part of the matrix in any desired proportion and can be made to exist within the block along the entire spectrum from 'perfectly homogeneous distribution' to "clusters of grains disseminated at random throughout'. MACS can then gather and analyze a sample (which is a grab sample) from any randomly selected location within the rock block. This process can be replicated a large number of times. thereby providing a large number of pyrite (or sulfur) determinations which can then be subjected to statistical analysis.

An Example of the Simulation

The MACS software is given the following set of instructions:

(1). generate 11 blocks of rock

(2). each block is to contain 7% total iron disulfide

(3). cluster the iron disulfide in each block according to the following scheme:

BLOCK NUMBER	degree of iron disulfide CLUSTERING	COMMENTS
1	0%	perfectly homogeneous
2	10%	
3	20%	
4	30%	
5	40%	
6	50%	
7	59%	
8	70%	
9	80%	
10	90%	
11	100%	highest order of non-homogeneous

(4). Make the clusters of various sizes (10 to 250 microns).

(5). Select 10000 samples from each strata block, analyze them for pyrite (or sulfur) content, and report the results.

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RESULTS

The distribution curves for the results of the iron disulfide analyses generated by the computer can be seen in Figure 9. Each distribution curve represents a different degree of clustering of iron disulfide. The perfectly homogeneous block (0% clustering) is the distribution farthest to the right. It should be noted that this distribution of has the general appearance of a normal or Gaussian distribution as well as having a numerical average and median (from the 10000 analyses performed) nearly equal to the 'true' amount of iron disulfide in the sample (ie. *l* wt%). Each successive distribution curve going to the left represents an additional 10% iron disulfide clustering. The degree of iron disulfide clustering within the block definitely influences the analytical distribution of results. Although this family of distribution curves resembles a family of distribution curves known as 'chi-square' (see Figure 10), they are, in fact best described mathematically and logistically by a family of distribution curves known as the Poisson distribution (see Figure 11). The overall appearance of the distribution curve representing 0% iron disulfide clustering to that of a normal or Gaussian distribution is simply a special case of a Poisson distribution.

Poisson distributions and Poisson events have long been used to predict catastrophic and other random events such as radioactive isotope disintegration. Numerous natural Processes yield results that have Poisson Distributions. The results of the dart throw scenarios are also Poisson Distributions. In the case of iron disulfide analysis, a Poisson distribution is most descriptive because it offers an insight into the random processes (iron disulfide formation) that occurred millions of years ago. Such a random, three dimensional process is, by definition, a Poisson process.

A Poisson distribution has the general mathematical formulation:

$$P(X) = \frac{e^{-\mathrm{lambda}}\,(\mathrm{lambda})^{X}}{X\,!} \qquad \text{EQUATION 1}$$

Figure 11 is a family of Poisson distribution curves with various lambda values. The X value for each curves corresponds to a wt% iron disulfide (1% - 7%). The resemblance to the family of distribution curves shown in Figure 9 is not coincidental. Iron disulfide clustering affects the distribution of analytical results by influencing the lambda value in equation 1. This can be seen in table 4 as well as Figure 12.

Table 4

Degree of iron disulfide clustering and corresponding lambda values for iron disulfide analytical distribution curves.

CLUSTER	LAMBDA
0	7.02280
10	6.40201
20	5.86022
30	5.35436
40	4.85578
50	4.28981
59	3.75828
70	3.27499
80	2.74911
90	2.29908
100	1.75751

Keep in mind that the total iron disulfide content of each strata block was 7% . The degree of clustering has not only affected the lambda of the Poisson distribution function, but also the median ~50-th percentile) value for iron disulfide obtained from 10000 analyses. The degree of clustering of iron disulfide has moved the 'true' value of 7% iron disulfide into regions of low Probability. If the median iron disulfide value of the analytical results performed on the strata block corresponding to 40% clustering is used, an analyst would be 'locked into' a value of 4% iron disulfide, which is a significant underestimation. A plot of the median values for the % iron disulfide and their relation to the degree of clustering can be seen in Figure 13. The variance (represented by the standard deviation) as it relates to the degree of clustering can be seen in Figure 14. Not only has iron disulfide clustering affected the median but it has also affect the variability of analytical results. The same effects do not necessarily hold for the mean or average value of iron disulfide. However, the high variances associated with high degrees of clustering preclude the use of the mean derived from a small number of sampling events as a measure of the 'true' concentration of iron disulfide minerals.

Results similar to the these cited above can be noted from a large number of actual field results which evaluated the total wt% sulfur of the various rock types associated with coal (see Figures 15 and 16). The left skewness of these distributions does not necessarily indicate an overall underestimation of sulfur for -all of the samples in the database. First the distributions are comprised of samples taken from many different locales and secondly, as previously indicated the true population of iron disulfide is not known for any of these samples; There is simply no way to derive the 'true' value.

The authors were Provided with a database representing 505 analyses performed on a single gobpile which has a distribution similar to a pyrite block having a high degree of clustering (Figure I7). A gobpile contains many different materials with a high range of pyrite contents. Because the placement of material in a gobpile is random, this could be treated as a large scale clustering scenario. Utilization of the distribution of these analytical results yields more information than the numerical average.

A sulfur distribution was obtained from the Coal Reclamation Information System database on the shale and sandstone rock units closest to and above the Upper Freeport and Pittsburgh coal beds. These can be seen in Figures 18-21. It should be noted that these shale and sandstone layers may or may not be continuous throughout the entire coal bed and could represent different sedimentary deposition sequences.

How can the knowledge of mode of pyrite distribution within a rock. the analytical results of pyrite contained in the rock, the sampling method, and the distribution of analytical results help the analyst, by indicating what must be done to produce a more accurate determination for wt% iron disulfide in a rock unit? First, a large number of analyses must be made. The number of analyses necessary is that which would allow the analyst to see a definite distribution of analytical results. Analyzing numerous small subsamples rather than a relatively large sample taken from a core or rock layer should aid in revealing the analytical distribution results. At the same time, such a multiple sampling would also the sampling method and analytical scheme to resemble a Markov process. When the distribution of the analytical results are plotted a distribution resembling the left skewed Poisson distribution curves shown in either Figures 9 or 11, will indicate that the median will underestimate the true amount of iron disulfide in the rock unit and that the mean will be associated with high variability. Figure 22 shows a plot of the 75-th Percentile 'as it relates to iron disulfide clustering. For highly skewed analytical distributions a higher percentile will yield results more reflective of the distribution mode of iron disulfide within the rock.

CONCLUSIONS

The following has been substantiated:

(1). Iron disulfide minerals are rarely distributed homogeneously in a rock unit.

(2). The degree of non-homogenity (clustering) of iron disulfide minerals effects the distribution of analytical total ,sulfur determinations. Clustering causes the analytical median values to be lower than the true value. In addition, the variances are too high to ascertain a reliable average from a small number of sampling events.

(3). The distribution of total sulfur analyses contains more information about the rock unit itself than any numerical average. If a <u>high</u> degree of clustering is suspected, then the a higher percentile would be more indicative of the true amount of iron disulfide in the material.

(4). Acid mine drainage has been reported to occur even though overburden strata have been determined to be low in total sulfur. The results of this study, indicate a strong possibility that the sulfur content of these strata samples were mis-identified as being low and the rock subsequently identified as being non-toxic due to iron disulfide clustering.

(5). Sampling on the magnitude of a drill core is a Markov Process but the sample preparation is such that the grinding and mixing of material turns a heterogeneous sample into a homogeneous material resulting in a loss of information and increase in knowledge entropy concerning the system in question.

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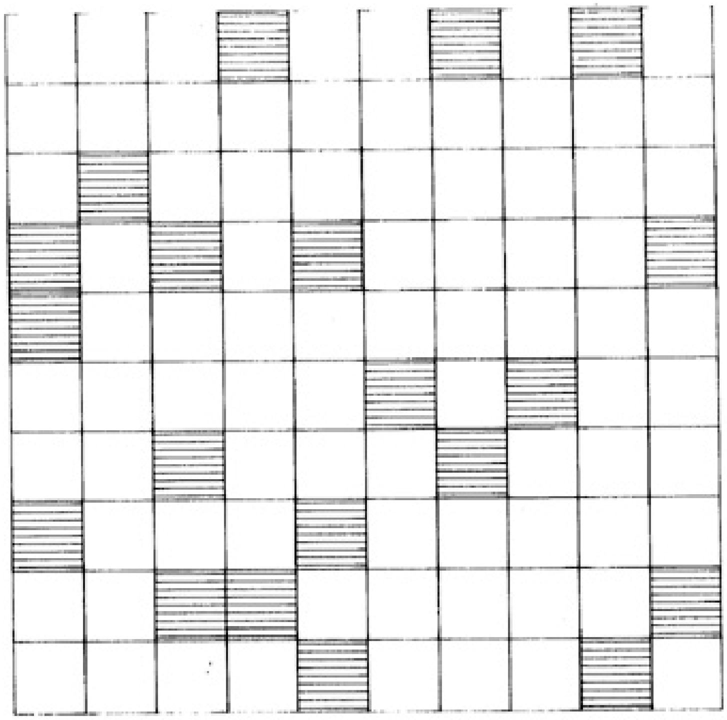

Figure 1

A UNIFORM grid in which 20% of the squares are black and these squares are homogeneously distributed.

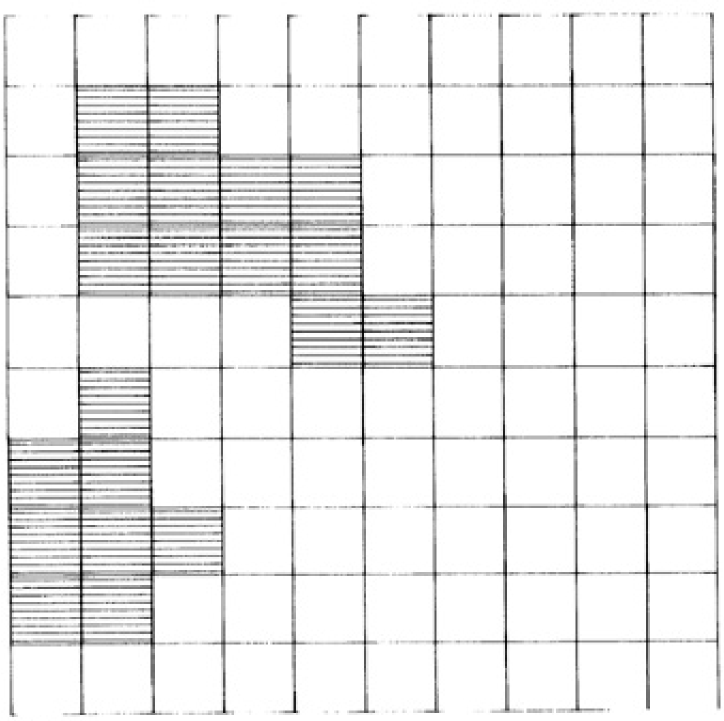

FIGURE 2

A CLUSTER grid in which 20% of the squares are black and these squares are 'clustered' rather than homogeneously distributed.

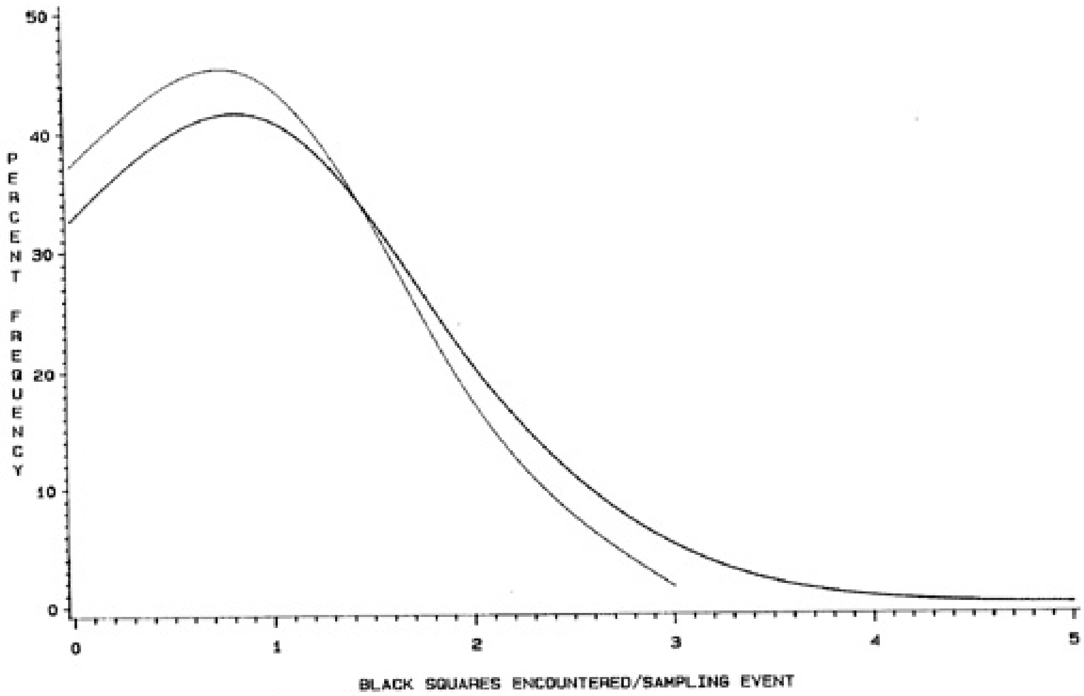

Figure 3

Distribution curves showing the percentage of black squares obtained using the 'Discrete' dart throwing sampling scenerio on both UNIFORM and CLUSTER grids.

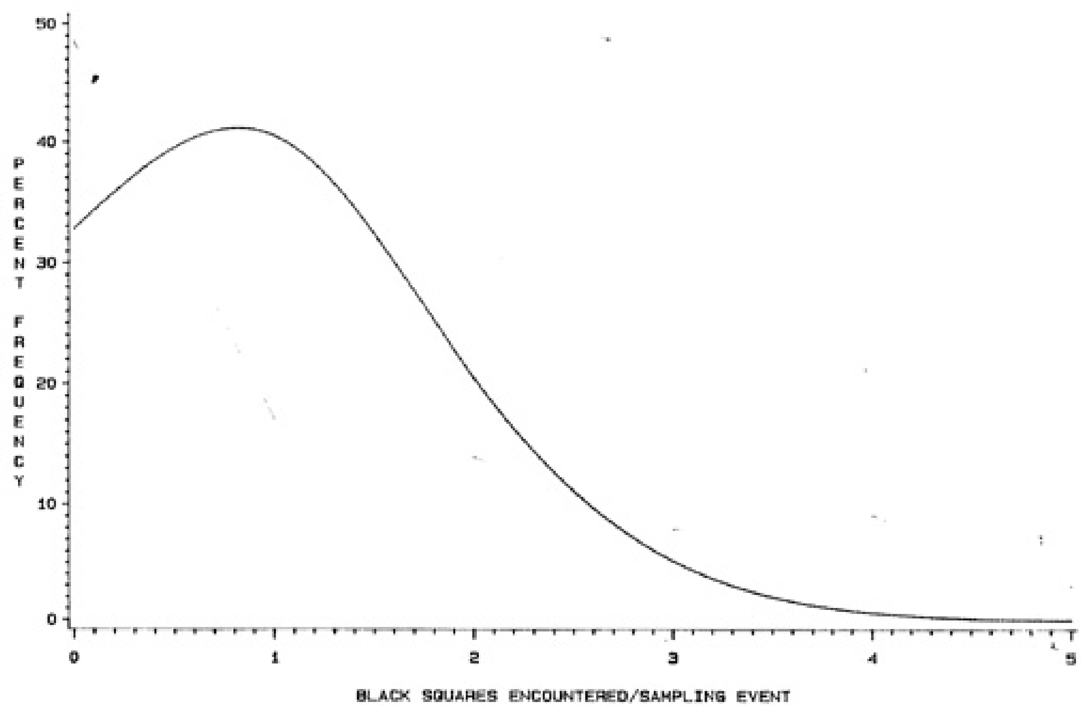

Figure 4

Distribution curves showing the percentage of black squares obtained using the 'Grab Sampling' dart throwing scenerio on both UNIFORM and CLUSTER grids. The curve similar to Figure 3 corresponds to the results representing the UNIFORM grid. The dissimilar, irregular curve correspond to the results representing the CLUSTER GRID.

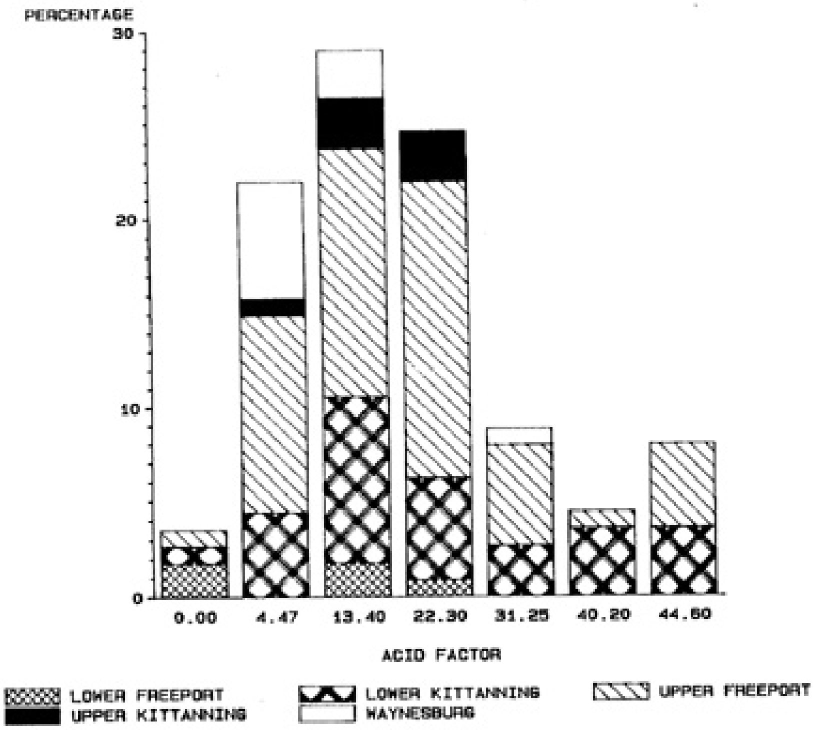

FIGURE 5

Histogram of the actual factor necessary to account for the acid produced in leaching studies on 108 toxic rock samples. 31.25 is the factor used by acid-base account.

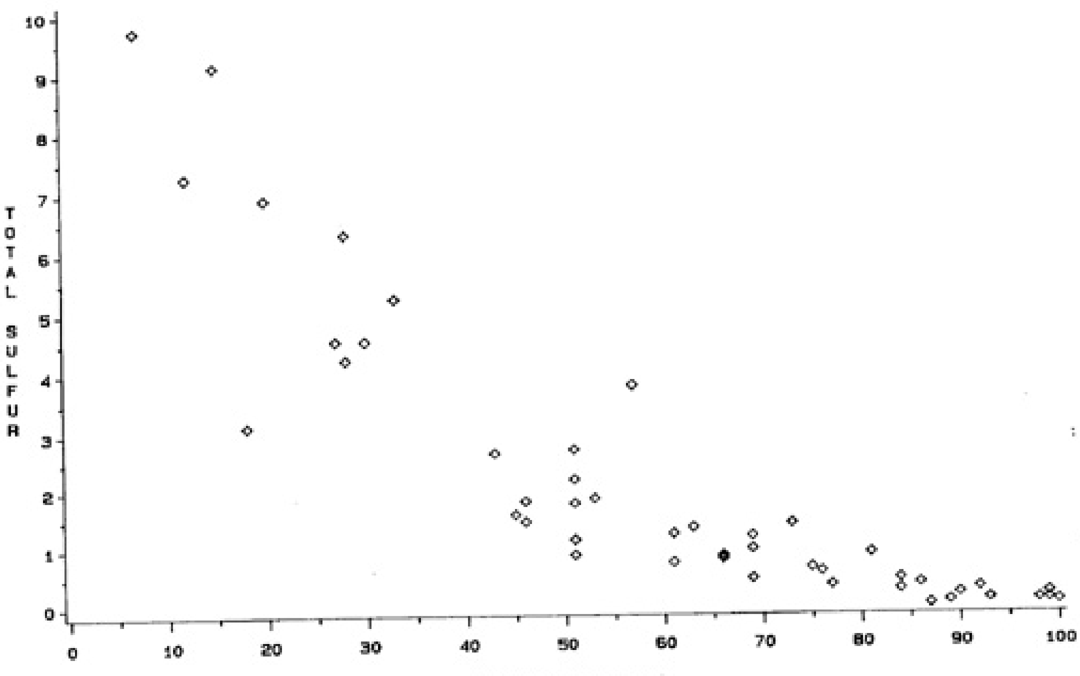

FIGURE 6

Relationship of isolated crystals of pyrite to total wt% sulfur analyses.

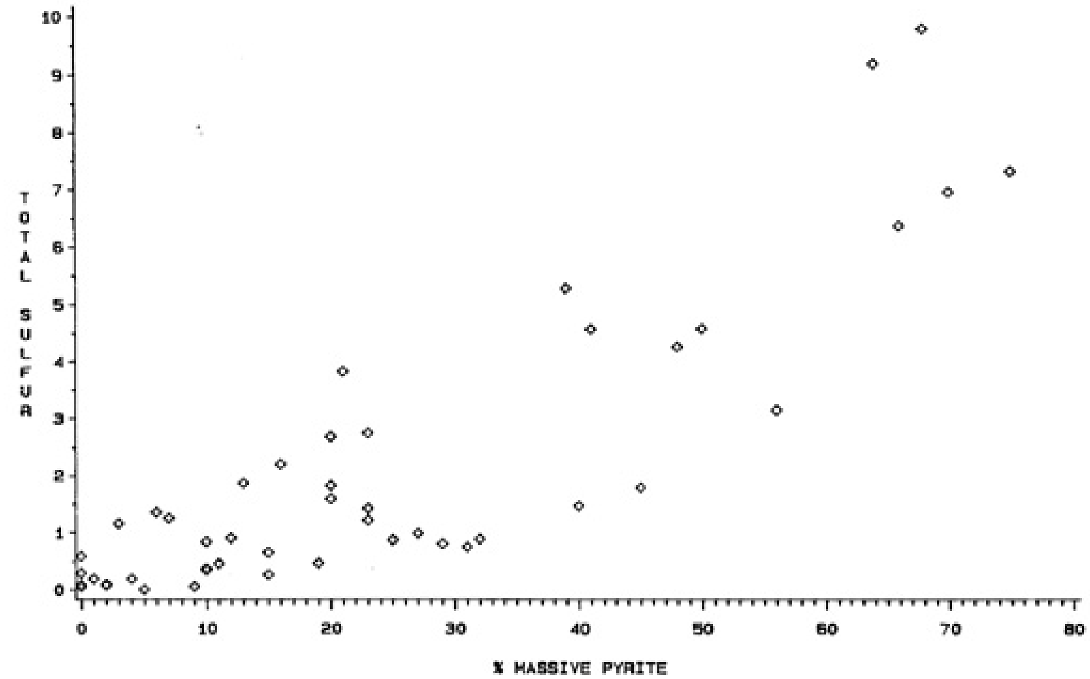

FIGURE 7

Relationship of massive pyrite to total wt% sulfur analyses.

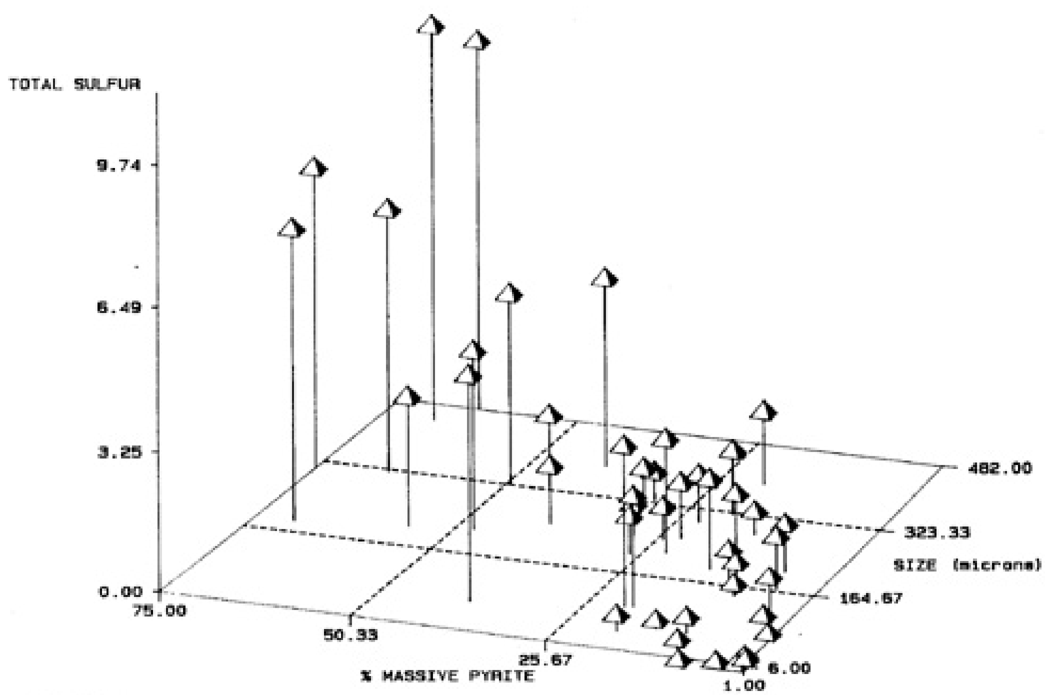

FIGURE 8

Interrelation between size and percentages of massive pyrite to total wt% sulfur.

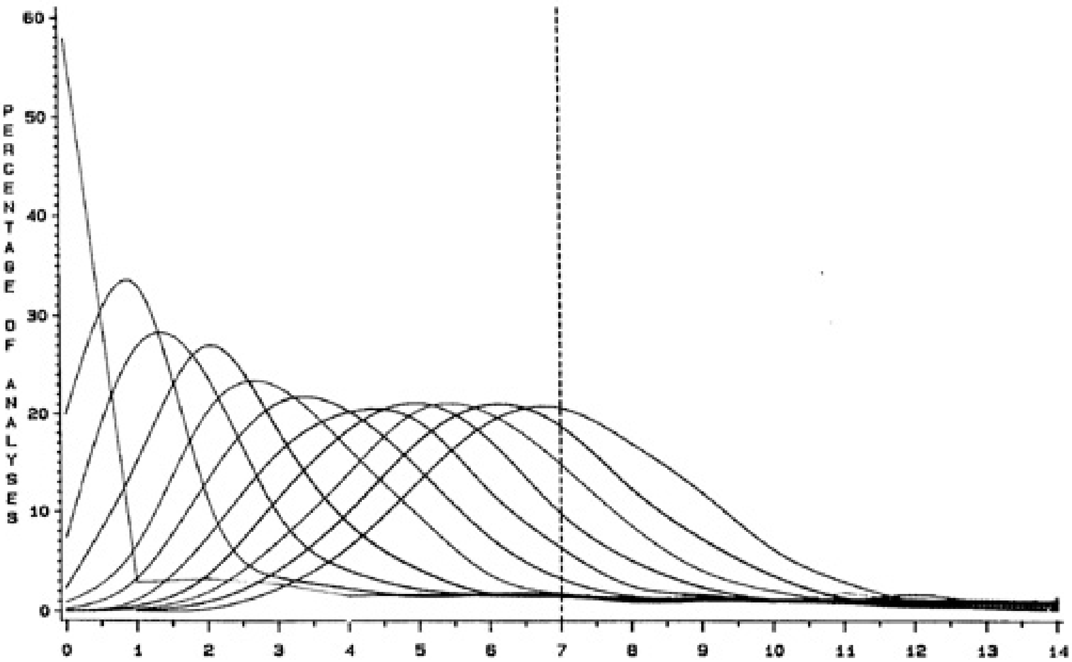

Figure 9

Distribution curves corresponding to 10000 iron disulfide analyses performed on each computer generated strata blocks. Moving from the vertical line (7% iron disulfide) to the left, each curve represents an additional 10% iron disulfide clustering.

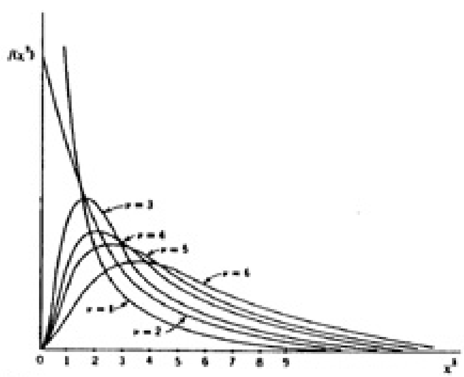

Figure 10 Chi-square distributions with ν degrees of freedom. (Adapted from *Elementary Statistics*, 4th ed., P. G. Hoel, Wiley, 1976, page 249.)

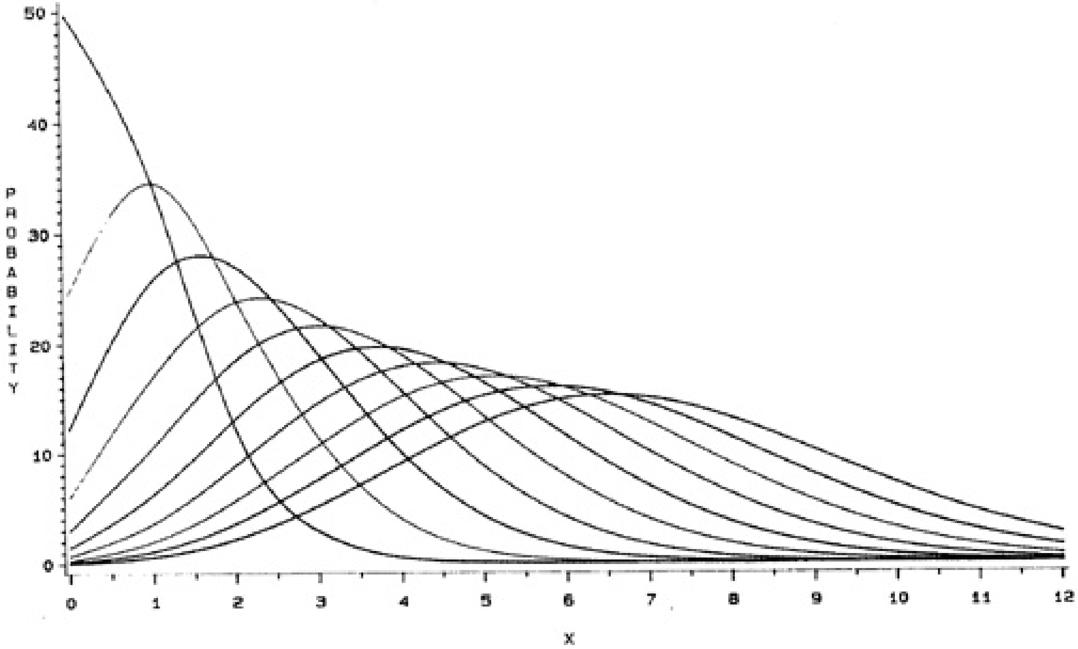

Figure 11

A family of Poisson Distributions curves corresponding to different lambda values.

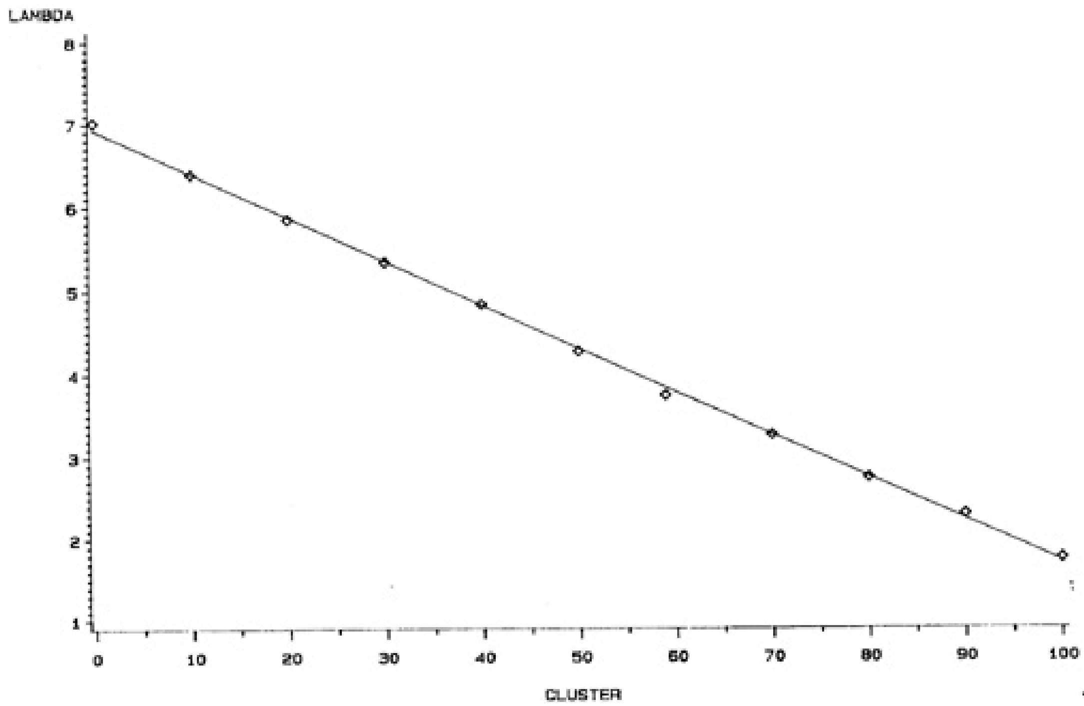

Figure 12

The relationship between the lambda term of the Poisson distribution function and the degree of clustering present in each of the 11 computer generated rock strata.

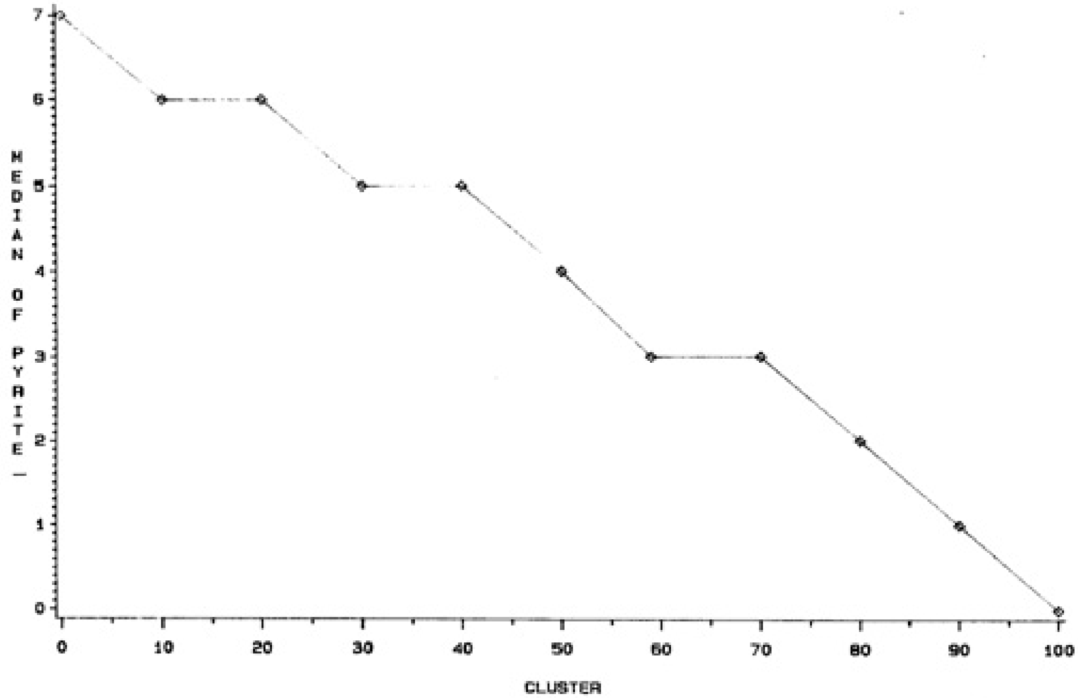

Figure 13

The relationship between the MEDIAN value of iron disulfide obtained in each computer generated rock strata and the degree of clustering present in the strata.

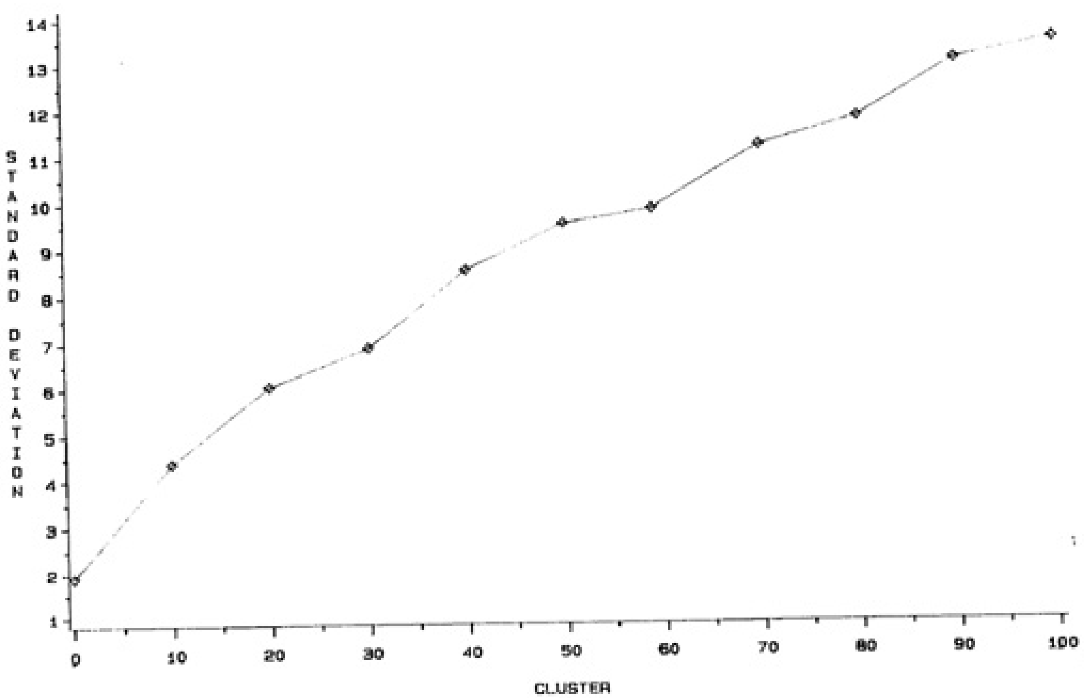

Figure 14

The relationship between the STANDARD DEVIATION (variance) value of iron disulfide obtained in each computer generated rock strata and the degree of clustering present in the strata.

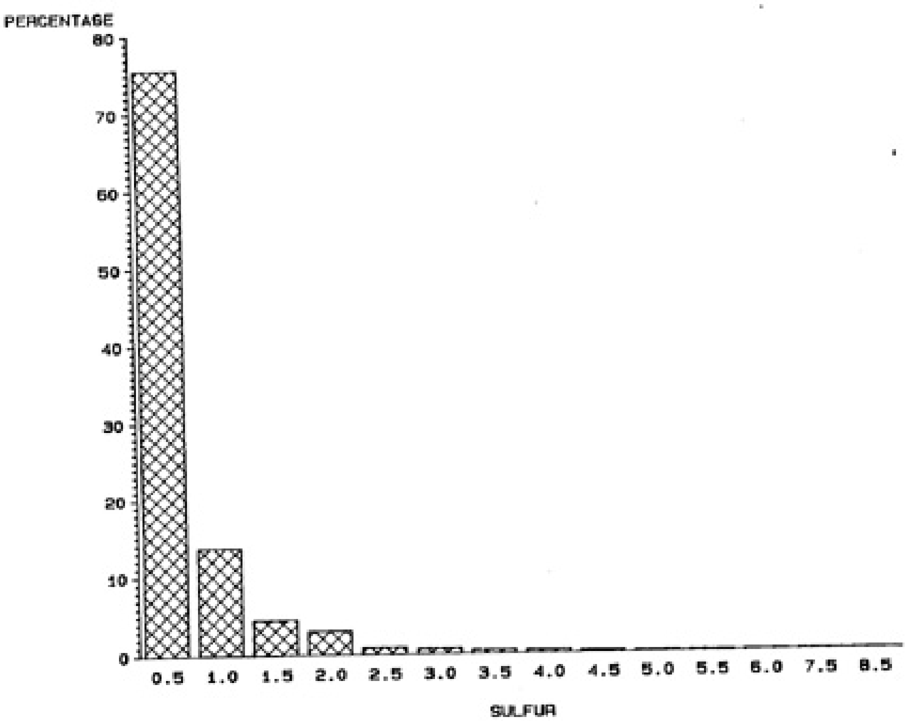

Figure 15

Histogram of the total sulfur distribution in SHALES for 1541 samples.

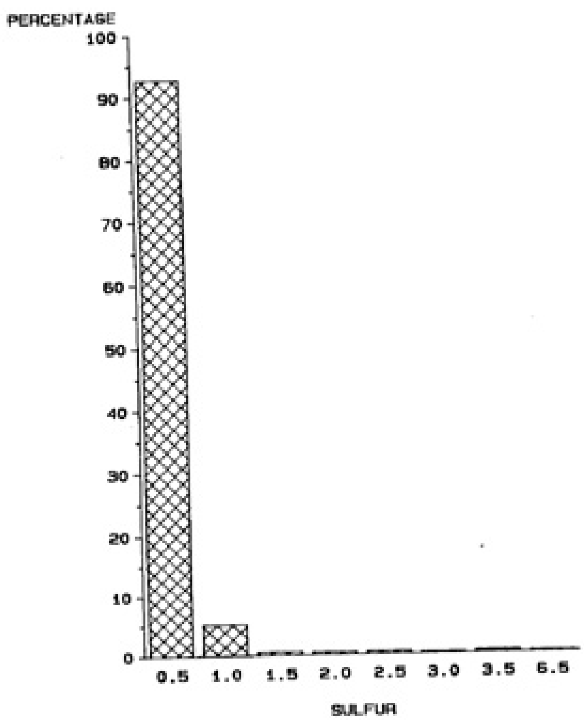

Figure 16

Histogram of the total sulfur distribution in SANDSTONE for 887 samples.

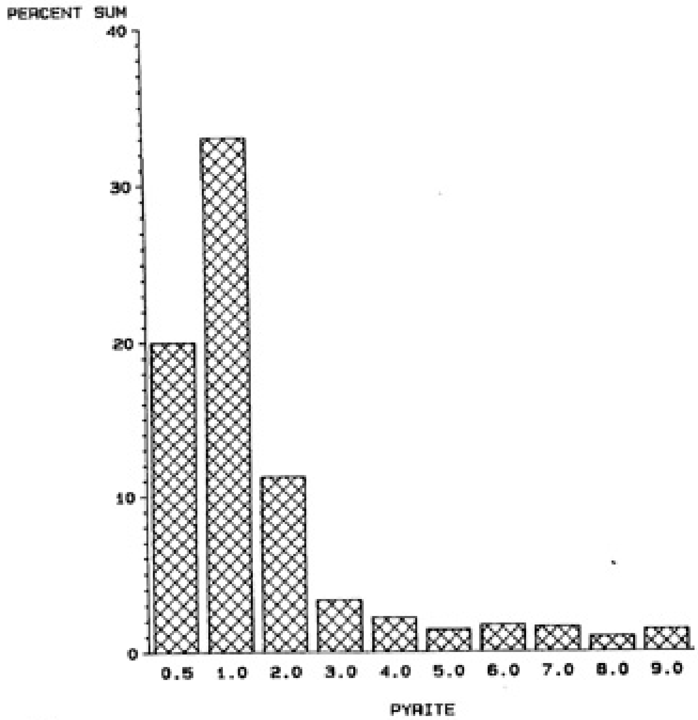

Figure 17

The distribution of 505 total sulfur analyses performed on a single refuse pile.

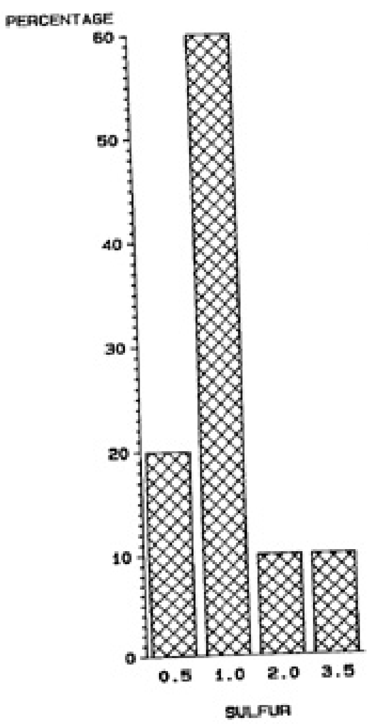

Figure 18

Histogram of the total sulfur distribution for the SHALE nearest to and above the Pittsburgh coal seam in northern West Virginia.

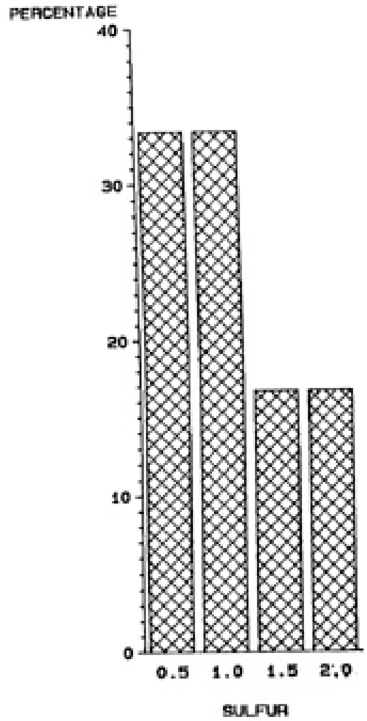

Figure 19

Histogram of the total sulfur distribution for the SANDSTONE nearest to and above the Pittsburgh coal seam in northern West Virginia.

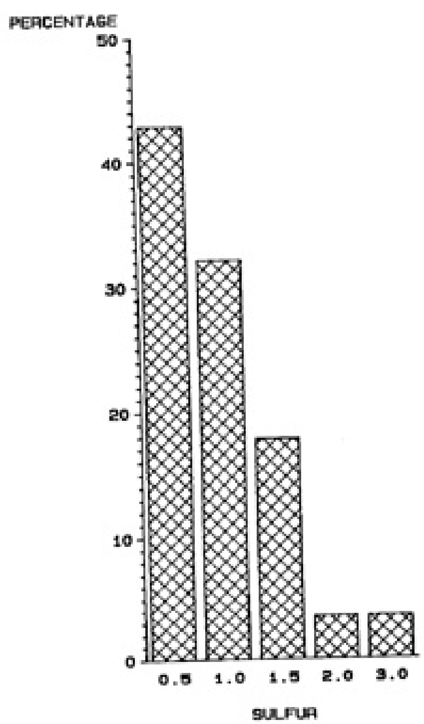

FIGURE 20

Histogram of the total sulfur distribution for the SHALE nearest to and above the Upper Freeport coal seam in northern West Virginia.

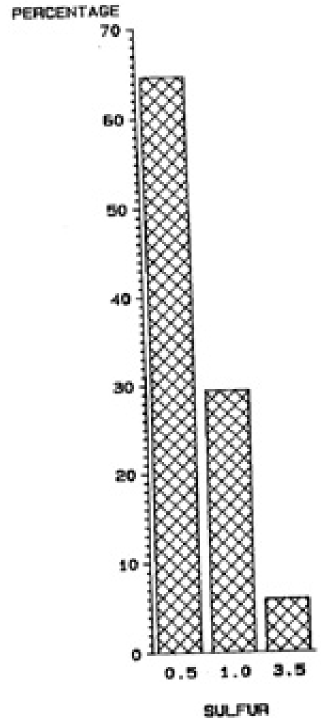

Figure 21

Histogram of the total sulfur distribution for the SANDSTONE nearest to and above the Upper Freeport coal seam in northern West Virginia.

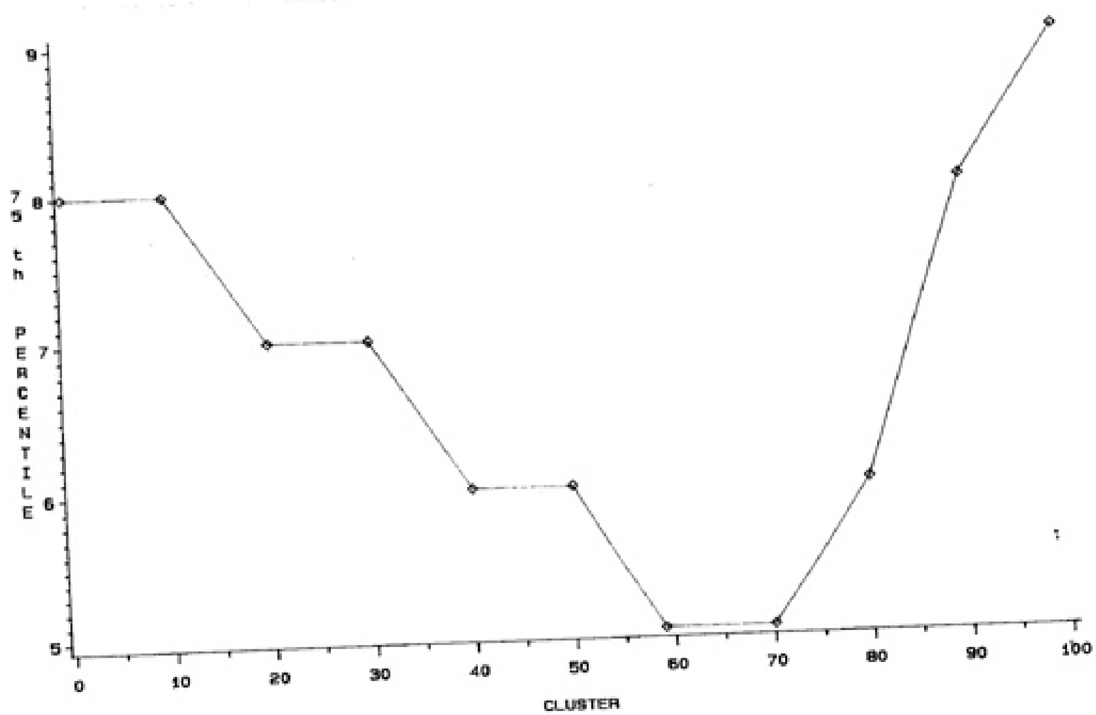

Figure 22

The relationship between the 75th percentile of the iron disulfide analysis results and the degree of clustering.