

Using Mössbauer Spectroscopy to Identify Indiana Oil Shales

An Honors Thesis (ID 499)

By

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I would like to give special thanks to Dr. Ruth Howes who has been a great help and inspiration to me during the past three years as well as my dutiful advisor for my thesis this quarter. Also, I would like to thank Kevin Bryan for his assistance in gathering the Mossbauer data used in this study and for drafting the final copies of Tables 1-5 in this paper.

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Purpose of Investigation:

Oil shales are recognized as being a potential source of petroleum for the immediate future. Indiana may have a source of valuable oil in its New Albany Shale which is distributed throughout the southern and western regions of Indiana. Shales are sedimentary rocks formed in shallow seas which are mixtures of inorganic minerals and organic materials. The organic matter contained in the oil shales is mainly kerogen, an insoluble solid material which can be extracted from the rock and refined to produce petroleum products. Kerogen is formed from the decomposition of plants buried in sediments. The process by which plant materials decompose and reform into kerogen as the sediments are compressed into shale is not well understood. In particular, the minerals in the shales which surround the organic material may or may not play a catalytic role in kerogen formation.

Investigations by the Indiana Geological Survey have shown that the New Albany Shale has a number of characteristic rock formations which reflect the organic content of the shale. There is a black shale rich in organic material with a high potential for petroleum development, a greenish-gray shale which is poor in organic material, and brown shales with an organic content which ranges between that of the black and the greenish-gray shales. Despite the obvious color differences in the shales, there are few mineralogical differences. For this reason standard mineralogical techniques cannot be used in trying to determine the relationship of the minerals present in the shales to the formation of kerogen.

It has been hypothesized that the organically rich oil shales were formed in an anoxic environment. The kerogen poor shales were formed in an environment high in oxygen which supported the presence of burrowing animals who consumed the plants before the kerogen could be formed. On this basis, it is expected that minerals in the organically rich shales

will be in a reduced oxidation state relative to those in the organically poor shales. (Maynard, 1982) This study reports an attempt to determine whether Iron-57 Mössbauer spectroscopy can be used to study the differences in the mineralogy of Indiana's New Albany Shales.

#### Background and Previous Studies of Oil Shales:

The New Albany Shale in Indiana is composed of dolomitic and siliceous brownish-black carbon-rich shale, greenish-gray mudstone and shale, and some amounts of dolomitic and quartzose rocks. There are five lithographically distinct regions where the different shales are located. The distribution is due to the marine environment in which the shale was deposited. Anoxic conditions caused by poor water circulation resulted in an accumulation of organic matter in the sediment. A dense mat of floating algae is proposed as the source of much of the organic matter. Such a mat may have increased oxygen reducing conditions by lowering the water circulation normally caused by wind. The plants might have also caused precipitation of carbonate by lowering the hydrogen ion concentration of the water resulting in withdrawal of carbon dioxide.

Studies indicate that the New Albany deposition ranges from the Middle Devonian to Kinderhookian time. The main source of the sediments was probably the erosion of the rising Appalachian Mountains. (Lineback, 1970)

The two categories of New Albany Shales are the black to brownish-black shales and the greenish-gray shales. The brown-black and black shales make up 65 to 80 percent of the shales. They usually have a high content of kerogen. The greenish-gray shales are less abundant at 6 to 18 percent and have only slight amounts of kerogen. (Shaffer and Pei-Yuan Chen, 1981) The brownish-black shale normally has as much as 20 percent by weight of

organic material and is considered carbon-rich. The organic material appears yellowish to reddish brown when sectioned, but depending on the amount, colors the shale various shades of brownish gray to black. (Lineback, 1970) Along with the organic material, the shale is composed of a high content of quartz, a lesser amount of clay minerals, as well as pyrite, marcasite, and carbonates (mostly dolomite but also ferroan dolomite and calcite). Feldspars are a minor portion seen only on x-ray patterns. Fine flakes of sericite are present in some samples. Traces of other minerals are also found. The mineral composition of the shale is rather constant throughout the shale for all except the carbonate content. (Shaffer and Chen, 1981) Iron in the shales is considered to be heterogeneous because of the highly variable content of iron sulfides. Pyrite and marcasite are common iron sulfides. Other iron-containing minerals are likely in small amounts. Siderite is found and ferroan dolomite is probably present. Magnesium is in excess of the requirement for carbonate and must be the illite, chlorite, or other clay minerals. Calcium is generally low except in carbonate-rich laminae. A few quartzose sandy carbonates have been observed. Manganese varies with iron but not always consistently. (Leininger, 1981)

Both the black and greenish-gray shales are composed of illite, some chlorite, and mixed-layer clay minerals. Mixed-layer clay minerals are slightly more abundant in the greenish-gray shales than in the black shales. Chlorite is more common in the coarser samples, and mixed-layer clay is more common in the finer matter. No significant difference in the clay-mineral composition was found between the black and greenish-gray shales. This suggests they are derived from the same material but deposited in different environments. Burrows are rarely found in the black shale but are common

in the greenish-gray shale. (Lineback, 1970)

A more detailed report of how the New Albany Shale was supposedly distributed and formed is presented in a portion of a study done in 1976 by the Illinois State Geological Survey. Detailed studies on the geology and geochemistry of 14 widely distributed shales from Illinois, western Kentucky, and south central Indiana have been done. A striking characteristic of the shales was the various distributions of invertebrate fossils and biogenic sedimentary structures. Although many properties of the shales, including mineralogy and grain size, vary in narrow ranges, the bulk of the rock varies greatly and was determined mainly by the activity of organisms, especially burrows. The presence of the burrows destroys primary sedimentary structures, creates swirl patterns in the sediments and reduces the amount and changes the composition of organic matter preserved in the sediment. It also affects the physical properties of shale.

According to this study, 3 factors affected the distribution of organisms and lithofacies. One is the energy of waves in very shallow water, particularly by the shore, where few organisms could survive the constant agitation. Next is the offshore oxygen distribution which varies from aerobic, where many burrows thrive, to dysaerobic to anaerobic, where few if any burrows exist, as the sea depths increase. Last is the bottom topography where the water depth controlled wave disturbance of the bottom affects distribution of oxygen and shale lithofacies.

The five general lithofacies described are: 1) fossiliferous limestone and dolomites, 2) highly bioturbated mudstones, 3) bedded shales, 4) thickly laminated shales, and 5) finely laminated shales.

The carbonate rocks of the fossiliferous limestone are a minor part



of the New Albany Shale. It was laid down in aerobic, shallow water. Burrows were able to survive in the areas most agitated by waves where carbonate is deepest.

Highly bioturbated mudstones form a major portion of the shales. They vary widely in grain size, in color, and in organic content. Most shales are silty, dolomitic, and greenish-gray in color. These were formed in dysaerobic, moderately shallow water and in quiet waters.

Indistinctly bedded shales in the New Albany are usually dark greenish-gray to olive gray and are slightly higher in organic content than the bioturbated mudstones. They contain silt-size or coarser material and contain no fossils. There is much burrowing. Thin interbedding of burrowed, gray shales with laminated black shales is common in several parts of the New Albany Shale. The mineralogy and grain size of the greenish-gray and black shales are about the same. They differ only in organic content and the degree of bioturbation. The color difference of the interbedded shales is therefore probably due to burrows made by animals consuming the sedimentary organic matter and, to a lesser degree, oxidation of the remaining organic matter after the burrowing animals passed through the sediment.

The thickly laminated shales were laid down in an anaerobic environment where water was deep and quiet with occasional currents. They are high in organic content and are black to brownish-black in color. The laminations are thick, irregular and widely spaced. Pyrite nodules are common. Silt layers found in some areas may be rippled or cross-laminated. Such sedimentary structures are indicative of bottom currents and are rare in the New Albany shale.

The finely laminated shales are brownish-black to grayish black,

high in organic content, and pyritic. The sediments are completely undisturbed by burrows, and these shales were at anaerobic, deep, very quiet waters which were virtually free of oxygen and burrows. (Cluff, 1980)

From these and other studies it has been hypothesized that the carbon-poor green-gray shales were deposited in water with oxygen where burrowing animals ate the plants before organic matter could be formed. The carbon-rich black shales were deposited in an anoxic environment in water containing  $H_2S$  which further reduced the oxygen content. Organic matter was allowed to collect and form kerogen here. (Maynard, 1982)

The organic matter in the shales is mainly an insoluble solid material called kerogen. There is no oil and little extractable bitumen naturally present in the rock. The shale which seems to produce greater yields are those in a shallow burial, evidently containing an immature stage of kerogen evolution before catagenesis begins. Examination of oil shale kerogens show that some of them are almost entirely made of algal remains. Some others are a mixture of organic matter.

The chemical composition of organic matter from oil shales may vary to a large degree. A high hydrogen content is always found. The atomic H/C ratio ranges from 1.25 to 1.75. The oxygen content is variable. The atomic O/C ratio ranges from 0.02 to 0.20. Nitrogen is much less abundant and varies a great deal. The reasons for the different composition and structure of oil shale kerogen may be found in different organisms contributing to the shales. The amount of degradation versus preservation at the time of deposition may also be important. The composition of kerogen in respect to hydrogen and oxygen determines the oil-generating potential of a sediment. (Tissot, 1978)

### Principles of Mössbauer Spectroscopy:

Mössbauer spectroscopy is the resonant absorption and emission of gamma-rays. The discovery of recoilless nuclear resonance was made by the German physicist Rudolf L. Mössbauer in 1958. The following is a description of the events leading to Mössbauer's discovery, the theory behind his discovery, and the applications of his discovery.

#### (a) Events Leading to Mössbauer's Discovery

In the mid-1800's, Stokes found that solids, liquids, and gases, can absorb electromagnetic radiation and then immediately radiate it. This is known as fluorescence. Resonance fluorescence is a special case where the emitted radiation exhibits the same wavelength as the incident radiation. In optics, resonance fluorescence refers to light emitted when atoms have a transition from the excited (higher energy) state to the ground (lowest energy) state. In 1929, Kuhn proposed that nuclear processes follow the same principle. Resonance absorption could be produced with radioactive sources where radioactive transitions take place between the nuclear states of two nuclei of the same kind.

In 1953, the nuclear resonance fluorescence effect was observed by P.B. Moon. The reason for the large time span in finally understanding and observing this effect is explainable. Emission is when a free excited nucleus emits a gamma of energy  $E$  and falls to its ground (or any lower energy) state. Here the nucleus must conserve linear momentum. In doing this, it must recoil with an energy which is  $R = \frac{E^2}{2mc^2}$  ( $m$  is the mass of the recoiling nucleus,  $c$  is the velocity of light, and  $E$  is the total energy). The energy released in such a nuclear transition is then divided between the nucleus and the photon emitted in order to satisfy the law of conservation of momentum where  $E = E_\gamma + R$ .

Absorption involves a process opposite from that of emission. If a single nucleus is excited by a photon, it vibrates due to the energy of the photon. When it vibrates, the nucleus radiates electromagnetic waves which are gamma rays. The amplitude of the wave vibration gradually decreases as the energy imparted by the photon is released. Then when a single nucleus is excited, the photon striking the nucleus must have an energy  $E_\gamma = E + R$  to allow for the effect of recoil upon absorption. Low energy gamma transitions have a recoil energy of about  $10^{-2}$  eV to  $10^2$  eV. However, the natural width of the resonance is about  $10^{-8}$  eV. In quantum mechanics, resonance only occurs if the energy lines of the source and absorber overlap within their natural energy width. This indicates that by taking part of the energy of the gamma ray, the recoil destroys the resonance condition. This is why nuclear resonance absorption could not be observed for such a long time. Also, the Doppler effect produced by thermal motion usually broadens the gamma lines so that their width at room temperature is about  $10^{-1}$  eV. Due to this slight overlap of the emission and absorption spectra, the cross-sections for resonance were very small. Attempts were made by experimenters to deal with these problems, but the shifts in energy due to electron interaction with the nucleus were small and could not be seen unless the gamma ray spectrum was reasonably sharp.

(b) Explanation of Mössbauer's Discovery:

What Mössbauer discovered was that under the proper conditions, a certain fraction of nuclei which are bound in crystals do not recoil. Instead the crystal as a whole absorbs the recoil momentum and this results in a negligible energy loss by the gamma rays. This discovery allowed direct measurements of the widths of narrow transition lines as well as to

the observation of small energy shifts of emitted gammas due to nuclear and atomic forces.

This discovery is based on the idea that the energy of a gamma ray lost through recoil decreases as the mass of the recoiling body increases. Therefore, if the emitting or absorbing nucleus is tightly bound in a crystal lattice, the nuclear recoil momentum must be taken by the crystal as a whole. Since the mass of a crystal is very large compared to the mass of a single nucleus, the energy given to the translational motion of the center of the mass is negligible. If the nuclei were rigidly bound to the crystal, this energy would be completely negligible inside the lattice as it is for overall translational motion. However, the atoms are not rigidly bound to the crystals. They are arrayed in a lattice which is vibrating. The energy of the vibration is not fixed. If any energy addition to the system occurs when the nucleus is left with recoil energy due to the gamma rays emitted, the energy will usually increase the energy of the lattice vibrations. This indicates that the energies of the lattice are quantized. The energy is transferred to and from the lattice in units called phonons. Mossbauer discovered that in certain conditions the nuclei of the lattice may undergo transitions without creating or destroying lattice vibration or phonons. The term "recoilless" refers only to the absence of energy transfers to the lattice since momentum is transferred in recoilless transitions and in those that recoil. He also proposed a theoretical treatment of his observations where the lattice vibrations are assumed to appear from a set of harmonic oscillators with quantized energies and a spectra of vibrational frequencies. The Debye approximation is used to describe the spectrum.

There are several conditions in which recoilless nuclear resonance

absorption can be observed. The nuclei must decay to the ground state of a stable isotope so that absorbers are available. The binding energy of the lattice must be high and the energy of the gamma transition should be low in order to increase the probability that no phonons are created. A high-energy gamma ray is much more likely to change the binding forces within the crystal through recoil of an individual atom. The Mossbauer effect is also highly dependent on temperature. To minimize the thermal energy of the lattice, the experiments can be carried out near or below the Debye temperature.

The Mössbauer experimental techniques are fairly simple. Generally, the Mössbauer effect is found by measuring the absorption of a source emitting gamma rays in an absorber. The absorber is placed between the gamma source and a radiation detector. The source or the absorber is moved linearly at a constant acceleration. Different driving mechanisms are used to produce this velocity. When the radiation measured by the detector is plotted as a function of the velocity of the moving source or absorber, a spectra is obtained. Any motion of the absorber induces a Doppler shift in the energy of the gamma rays incident on the absorber. This energy is enough to affect and at higher velocities destroy resonance. As stated before, resonance occurs when the energy of the emitted gamma rays corresponds exactly to the excitation energy of the nuclei in the absorber.

One of the most convenient gamma source materials to use is iron-57. This source is derived from a radioactive source of the isotope cobalt-57 whose half-life is 270 days. As the cobalt nuclei decay, they change into excited nuclei of iron-57. The nuclide has a low energy gamma transition of 14.4KeV. Its low energy gives a small recoil energy of the

free nucleus and increases the probability of recoilless emission and absorption. The fairly long half-life of the state which is  $10^{-7}$  seconds means that the natural linewidth is narrow which is an advantage in detecting small energy changes. Also, the high Debye temperature of iron makes it possible to conduct experiments at room temperature. Iron-57 is also particularly useful for the study of geological materials because iron is common in nearly all geological materials. The properties of the iron-57 nucleus are thoroughly studied and documented.

(c) Applications of Mössbauer Spectroscopy:

Recoilless nuclear resonance absorption makes it possible to measure extremely small energy differences in systems due to the small line widths. This property allows for a broad range of potential applications. This technique is a powerful tool for research in nuclear physics, general physics, and solid-state physics. It is also of importance in fields other than physics such as chemistry and geology.

The importance of the Mössbauer effect in solid state physics is due to the large number of parameters that experiments in this field may involve. Many experiments can be performed which yield information about lattice properties, internal fields and the effects of impurities, and vacancies in the lattice.

In general physics, the best known application is in the measurement of the gravitational red shift of gamma radiation energy. This proves Einstein's equivalence principle by measuring the supposed weight of a photon and showing that photons in a gravitational field behave like particles having mass.

Application of Mössbauer in nuclear physics, which is what this investigation of oil shales involves, are of great importance for modern

theories of the chemical structure of compounds and metals. The three parameters that have immediate chemical applications which can be determined by Mossbauer spectra are the isomer (chemical) shift, quadrupole moment, and the magnetic moment. Figure 1 shows these various interactions and the spectral lines they produce. These three parameters are measured from the absorption spectra which when compared against the thoroughly studied properties of the iron-57 nucleus, present quantitative information on the chemical state of iron in the absorber.

The isomer shift of the center of the resonance spectrum measures the electron density at the site of the nucleus. Its value is characteristic of different iron-bearing minerals. The isomer shift is a shift in energy. This shift in energy occurs when the nuclear radius changes due to either the addition of one or more neutrons or when the nucleus goes from one energy state to another. In the nuclear isomer shift, the same nuclear transition is compared in two atomic systems which must have different radii and wave functions at the nucleus. Calculations are made from measurement of these energy changes.

The nuclear quadrupole moment reflects the deviation of the nucleus from spherical symmetry. The interaction of the nuclear quadrupole moment results in the splitting of the nuclear levels. This splitting produces an absorption doublet whose splitting measures the asymmetry of the electron charge distribution at the crystal sites where iron is bound. The magnetic moment interacts with the magnetic field that gives information about the magnetic hyperfine structure due to the atom's electrons. The interaction of the magnetic moment of the iron nucleus with the magnetic field produced by the electrons produces a six line absorption spectrum. Six lines are not obtained in the spectra of the



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shales, which were recorded at room temperature. (Frauenfelder, Wertheim, and DeBenedetti)

Iron constitutes several percent by weight of the shales and they are therefore suitable for study using Mossbauer spectroscopy. With Mossbauer, the oxidation state of the iron in the shales can be distinguished. When the Mossbauer effect is used in characterization of clay minerals, there is a large isomer shift and quadrupole splitting which is typical of ferrous iron in octahedral sites. Smaller parameters are typical of ferric iron in octahedral sites. The isomer shift is generally a more valuable parameter than the quadrupole splitting for distinguishing different states of iron since its parameter range is more defined than that of the quadrupole splitting as shown in Figure 2. This is a plot showing the normal ranges of variation of the quadrupole splitting (Q) and the isomer shift ( $\delta$ ) derived from data on crystalline and amorphous silicates. (Carroll, 1970)

In this study, 22 samples of New Albany shale consisting of a range of differing organic content were obtained from Nelson R. Shaffer of the Indiana Geological Survey as a continuation of a study done earlier in the spring of 1983 at Ball State University. These shales were crushed and formed into absorbers whose thickness was approximately 50 mgm/cm<sup>2</sup>. Data for the shales were recorded at room temperature and then calibrated against a prepared sample of enriched iron-57 of which a typical spectrum is shown in Figure 3.

Data points were obtained on a conventional constant acceleration Mossbauer spectrometer using a gas-filled proportional counter and a nuclear data multi-channel analyser. In this set-up the source moves with a constant acceleration for a certain time and the counts during

this period are recorded. With constant acceleration drives, small parts of the spectrum can be investigated with high accuracy. A loudspeaker was used as the acceleration drive. The absorber is placed between the counter and the source as shown in Figure 4. (Frauenfelder, 1962) The source in this study was cobalt-57 diffused into a palladium matrix to produce a source gamma with a single energy. Data were computer-fitted using a version of the variable matrix minimization procedure developed at Argonne and modified at M.I.T., Columbia, and Ball State.

Constraints were placed on half widths of the absorption doublet and further doublets were added to the model spectrum until further doublets failed to reduce the chi squared value of the fit.

### Results and Conclusions

In a preliminary study of the New Albany Shales, four samples (NS79-9, NS79-57, NS79-308, and NS79-309) were examined. The chemical data for these shales can be found in Table 1. These data were also obtained from Nelson Shaffer of the Indiana Geological Survey. The shale sample NS79-9 is a shale rich in kerogen while sample NS79-308 is a shale poor in kerogen. The weight percent of the total carbon content in the organic-rich shale is much larger than that of the oil-poor shale. The weight percents of carbon found in the carbonate minerals of the shale exhibits an obvious difference between the two shales. There is a lower percentage of carbon in the carbonate minerals in the organic-rich shale than in the organic-poor shale. The low percentage of carbon in the carbonate indicates that large amounts of organic material are present.

The Mössbauer data taken for the shales is included in Table 2 along with more recent data. These first four are listed first in the table.

Table 3 shows a typical Mössbauer spectrum where the absorption spectrum consists of two unresolved doublets. The narrow doublet is characteristic of ferric (oxidized) iron, while the wider doublet is characteristic of ferrous iron. The solid black line shows the computer fit used to distinguish between the doublets quantitatively. The first group of values in the table indicate the data from the narrow doublet representing the ferric iron, and the second group indicates the data from the wider doublet representing the ferrous iron.  $Q$  is the doublet splitting.  $S$  reports the isomer shift relative to metallic iron and the amounts of ferric or ferrous iron in the shale, assuming

that the absorption cross-section is identical for all chemical sites in the shale and that the iron content is proportional to the area of its characteristic absorption doublet. All quantities are reported in mm/sec  $\pm$  .10 mm/sec. It was expected before any analysis was done using Mossbauer techniques that there would be less oxidized iron than reduced iron in the organic-rich shale samples such as NS79-9 and that the situation would be reversed in organic-poor shales such as NS79-308. However, the results of this preliminary study contradicted this simple hypothesis since the experimental results of the four shales showed a higher percentage of oxidation in brown and black shales. Since this study involved only four samples, no general conclusions could be drawn concerning the mineralogy of the shales.

It was for this reason that 19 more shale samples were obtained from Nelson Shaffer which consisted of shales ranging widely in organic content as well as color. These shales were analyzed by again using Mössbauer techniques. The final measurements of the quadrupole splitting, isomer shift, and % absorption are reported in Table 2.

Several methods were tried to find some pattern in the data. Table 4 shows the range of the isomer shifts versus the quadrupole splittings for the predominant doublet and for the less predominant doublet. Data separated into two groups of points which are associated with the ferric iron or ferrous iron. The isomer shift presents a more defined separation of the two groups than does the quadrupole splitting. Some points such as those for NS78-88, NS82-45, NS83-706, and NS80-60 stray from where the majority of points lie in the ferrous group. This graph indicates that ranges of the ferric and ferrous groups are much as expected and shows an apparent relation between

the quadrupole splitting and the isomer shift in the individual doublets.

Table 5 shows a bar graph relating the % absorption of the ferric doublet to the shale color. The shale color was determined subjectively and placed in order of increasing color-determined organic content. As is clearly visible from the bar graph, there is no apparent correlation between data and color analysis of the shales. Thus, there is no correlation between the data and the organic content of the shale. Visual analysis of the shales as well as this bar graph indicated that the shale sample 882-4 is anomalous. This could be due to the pyrite and marcasite content which is clearly visible in the shale.

Finally, Table 6 show the relation between the % absorption of the ferrous doublet versus the % absorption of the ferric doublet. This graph reveals an interesting linear relationship well within the  $\pm 10\%$  error estimated for these values. The points are well distributed in a linear pattern. An attempt was made to color code the points according to whether they were from the gray, brown, or black shales, but again no correlation between color and % absorption was evident. Further analysis is needed to explain this linear relationship. A few of the aspects that can be examined are the geographical location of the shale, the geological conditions of the site from which the shales were gathered, and the pyrite content of the shales. This data is not presently available.

Due to the results of the analysis previously described, it can be concluded that there is no apparent correlation between the content of ferric and ferrous iron as determined by Mössbauer spectroscopy and the organic content of shales.

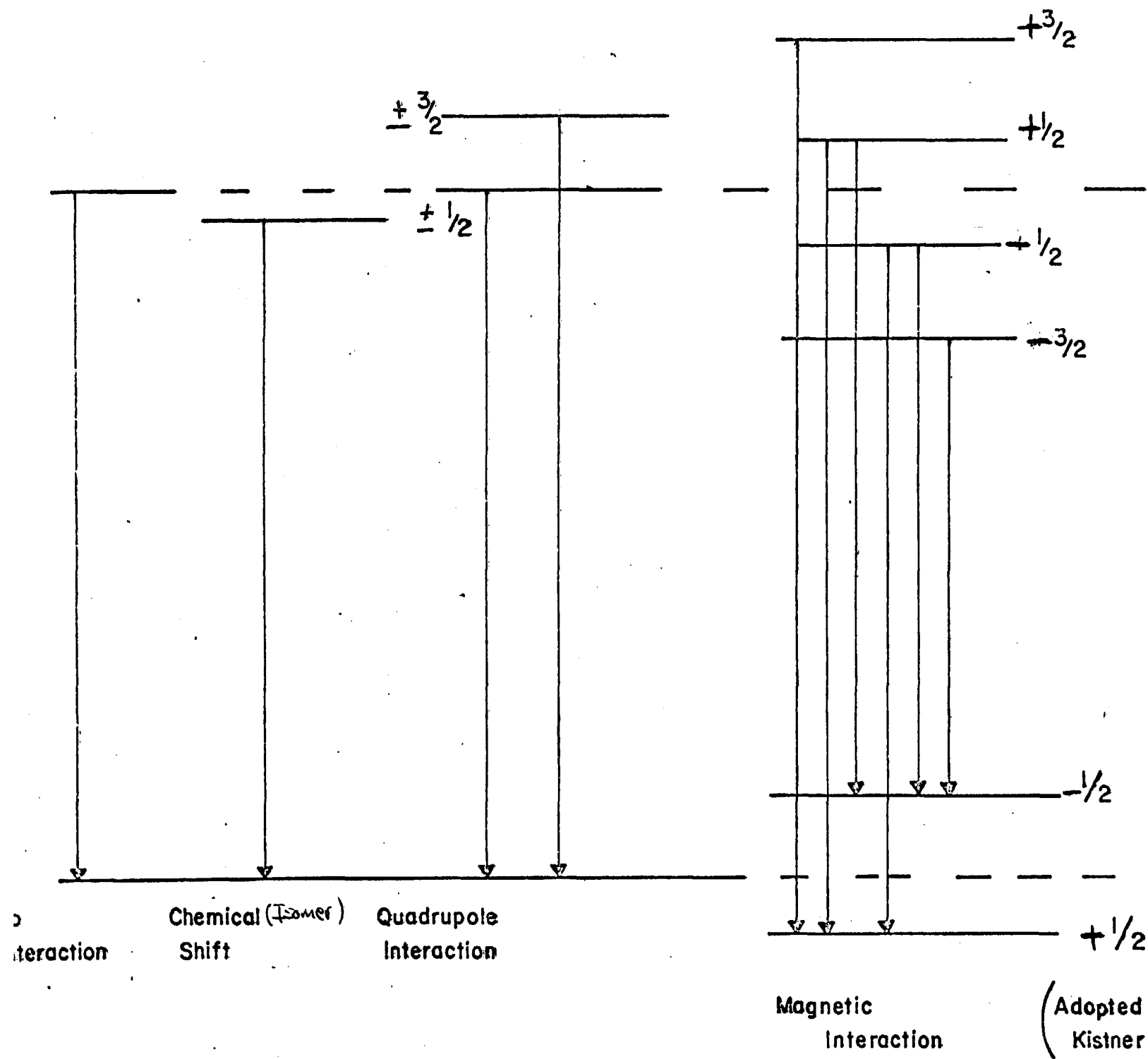
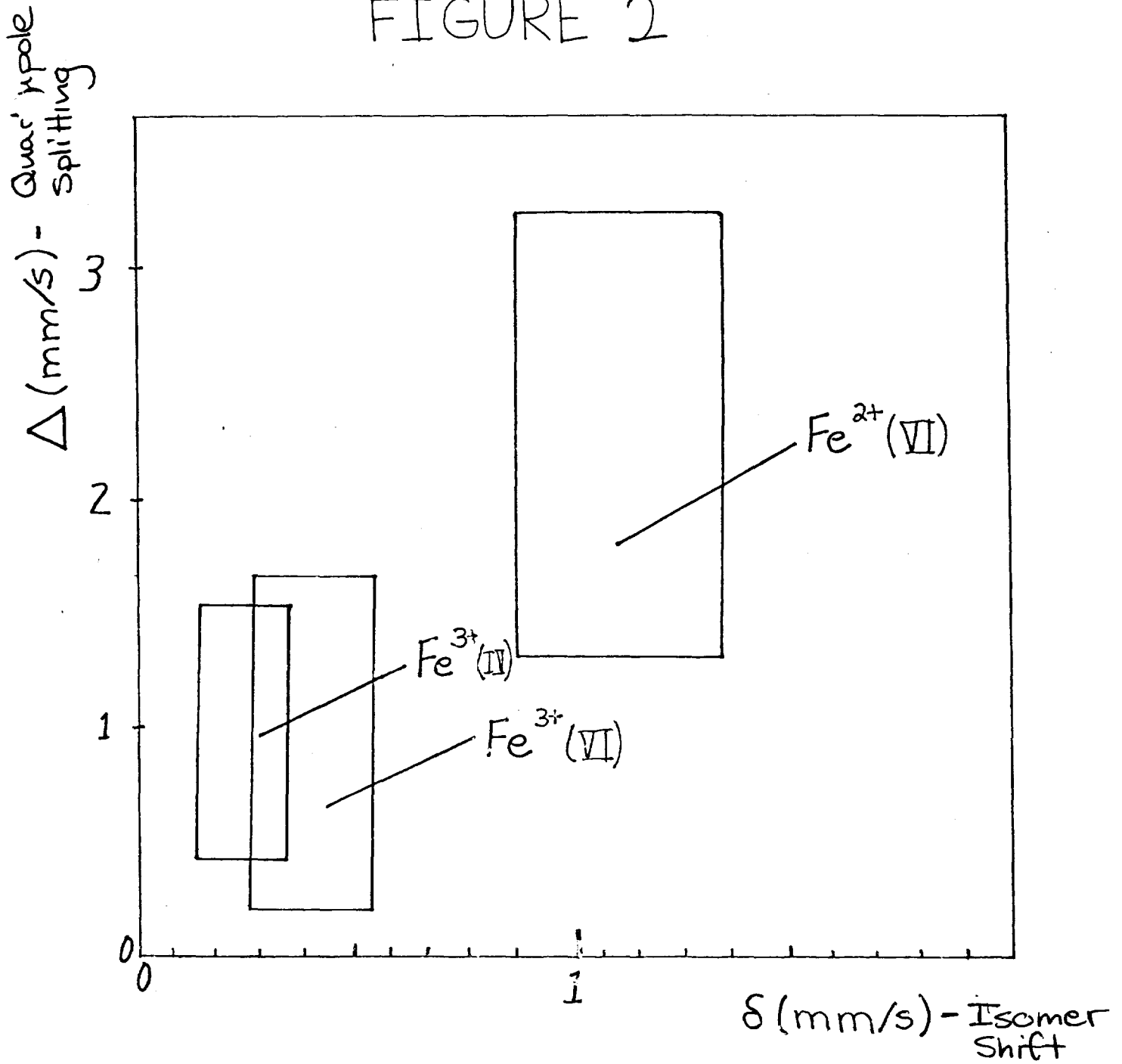


Figure 1.  
Spectral Lines Produced  
When  $^{57}\text{Fe}$  Interacts  
with its Environment

(Adopted from  
Kistner and Sunyar)

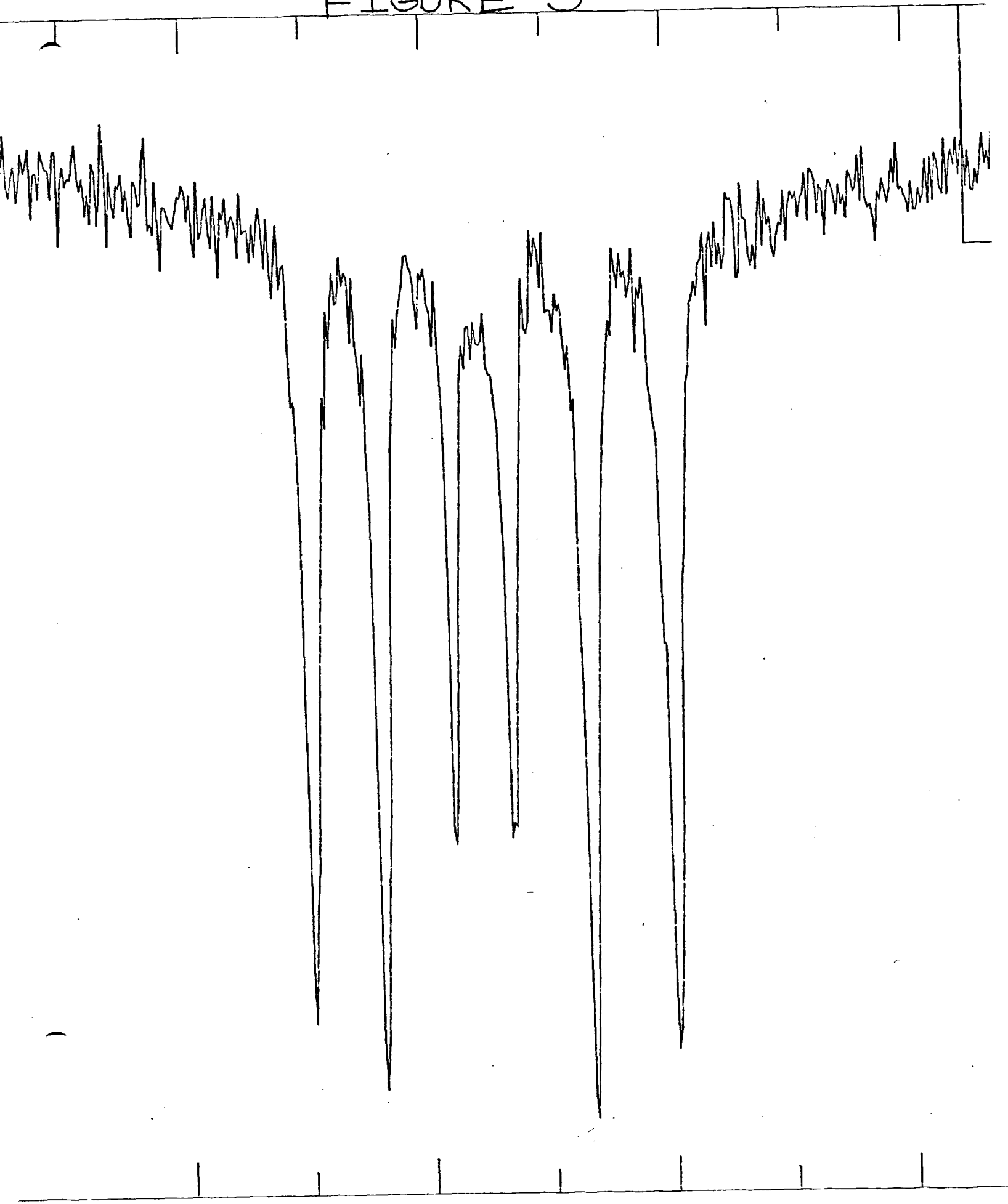


FIGURE 2

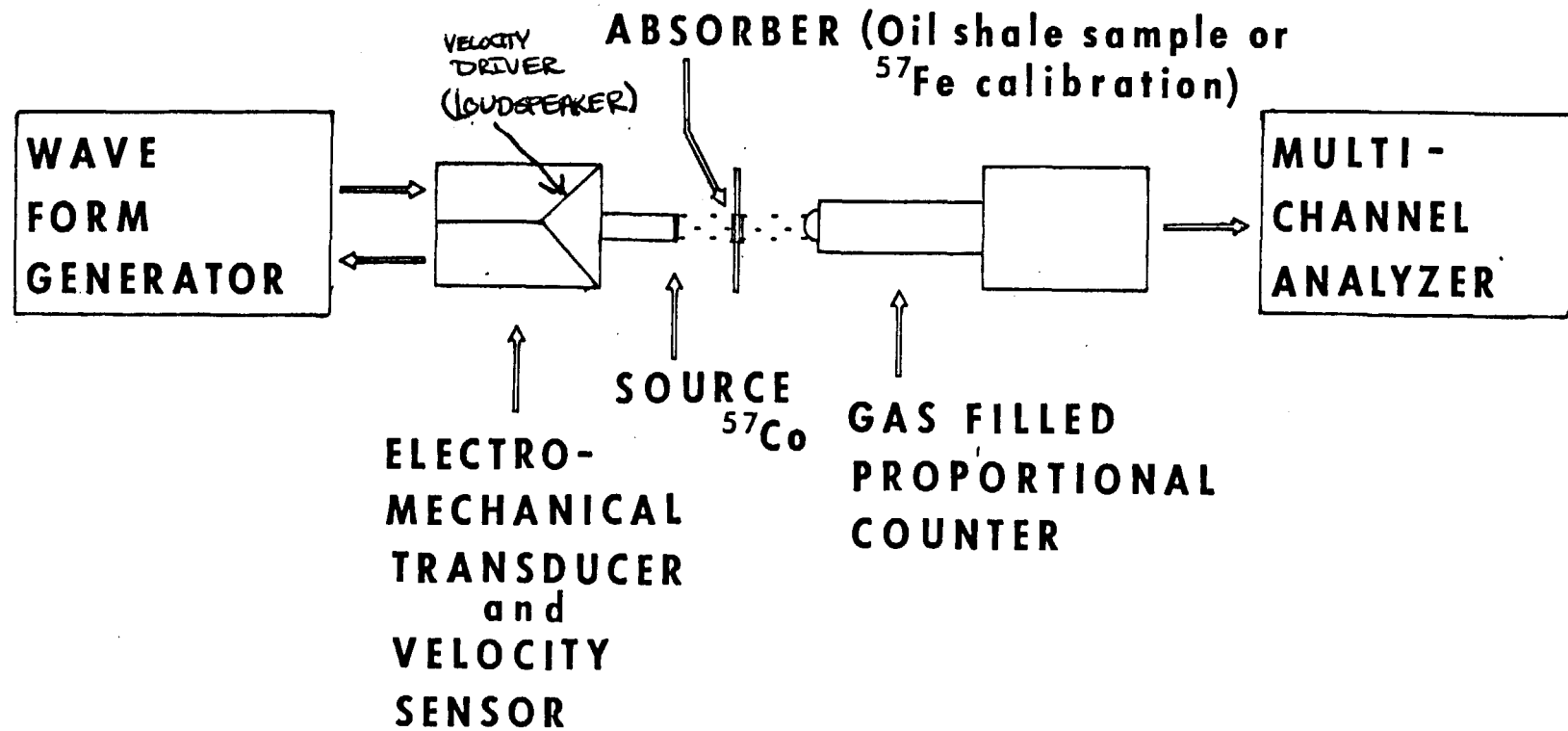


Ranges of variation of the chemical shift and quadrupole splitting for iron in different charge states.

FIGURE 3



# FIGURE 4



LABORATORY SET-UP

# TABLE I

## Chemical Data on Shales from Preliminary Study

<u>Weight Percent of:</u>	<u>C</u>	<u>H</u>	<u>N</u>	<u>C in CO<sub>2</sub></u>
NS79-9	24.15	2.19	1.20	.05
NS79-57	9.42	1.41	.35	.68
NS79-308	2.31	.53	.10	.74
NS79-309	8.56	1.15	.27	.12

# TABLE 2

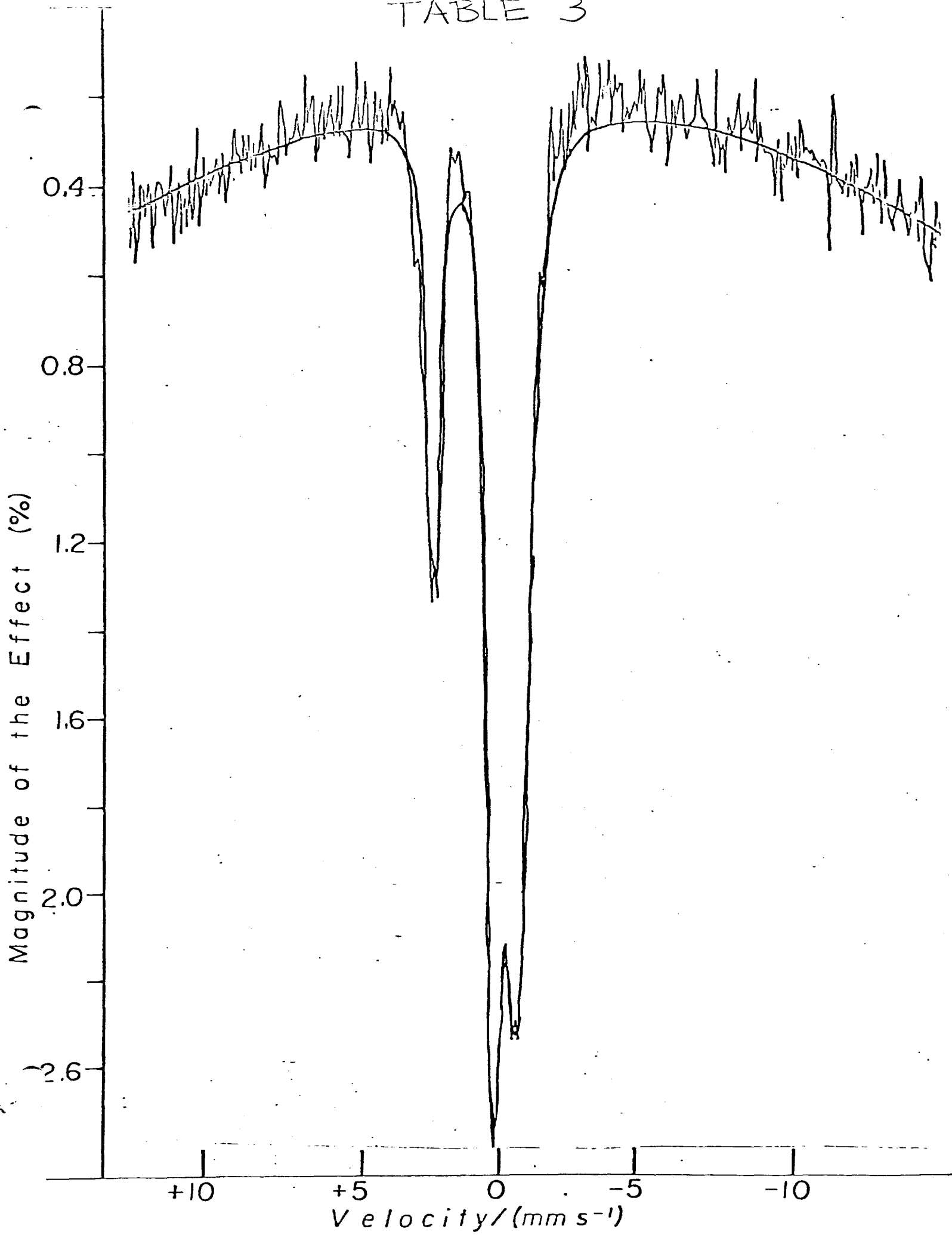
## Mössbauer Parameters for Shales \*

Sample	Q <sub>1</sub>	δ <sub>1</sub>	%	Q <sub>2</sub>	δ <sub>2</sub>	%
NS79-9	.69	.30	68	2.81	1.14	25
NS79-57	.68	.31	70	1.89	1.23	30
NS79-308	.50	.43	25	2.56	1.12	74
NS79-309	.76	.32	63	1.95	1.52	29
NS79-16	.79	.26	74	2.29	1.40	18
NS79-88	.42	.17	65	2.07	.60	31
NS79-143	.62	.33	81	2.65	1.04	13
NS79-149	1.00	.37	63	2.15	1.37	37
NS79-249	.55	.34	73	2.29	.93	16
NS79-302	.70	.36	75	3.13	1.16	13
NS80-60	.80	.21	77	.99	1.68	23
NS80-70	.48	.37	16	2.66	1.14	49
NS82-18	.59	.35	85	2.77	1.07	15
NS82-33	.22	.36	24	2.45	1.01	76
NS82-40	.53	.14	66	2.04	1.20	34
NS82-44	.77	.41	86	2.91	1.05	13
NS82-45	.10	.23	45	.28	.77	55
NS82-84	.73	.23	34	1.97	1.20	66
NS82-125	.81	.49	61	.33	1.51	39
NS83-706	.29	.33	57	.32	.81	42
Z82-2	.98	.48	47	2.00	1.46	52
Z82-4	1.13	.34	49	.12	.32	44
Z82-6	.47	.41	37	1.45	1.18	63

\* All quantities reported in mm/sec  $\pm$  .10mm/sec unless otherwise noted

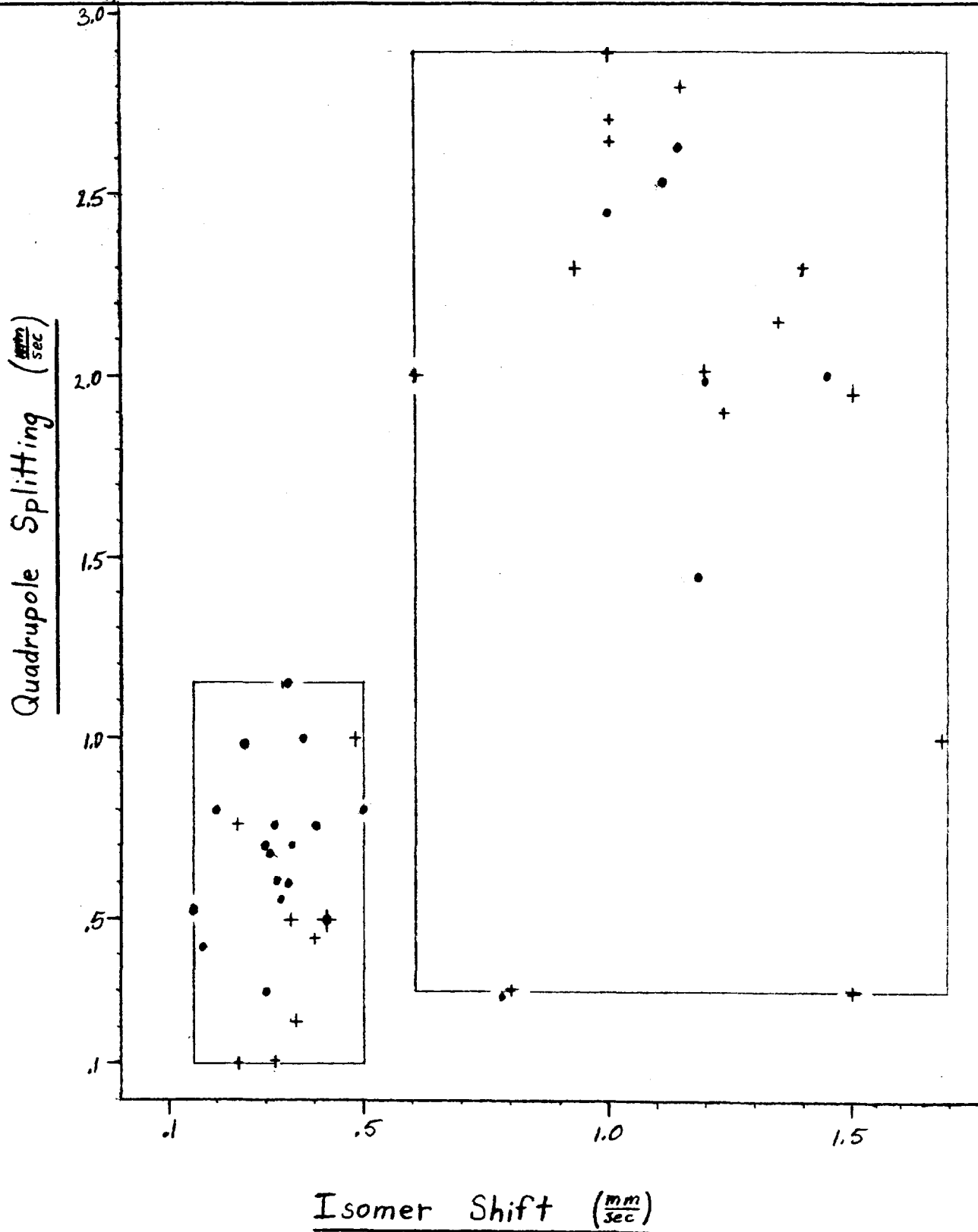
Isomer shifts ( $\delta$ ) are reported relative to metallic iron

TABLE 3



# TABLE 4

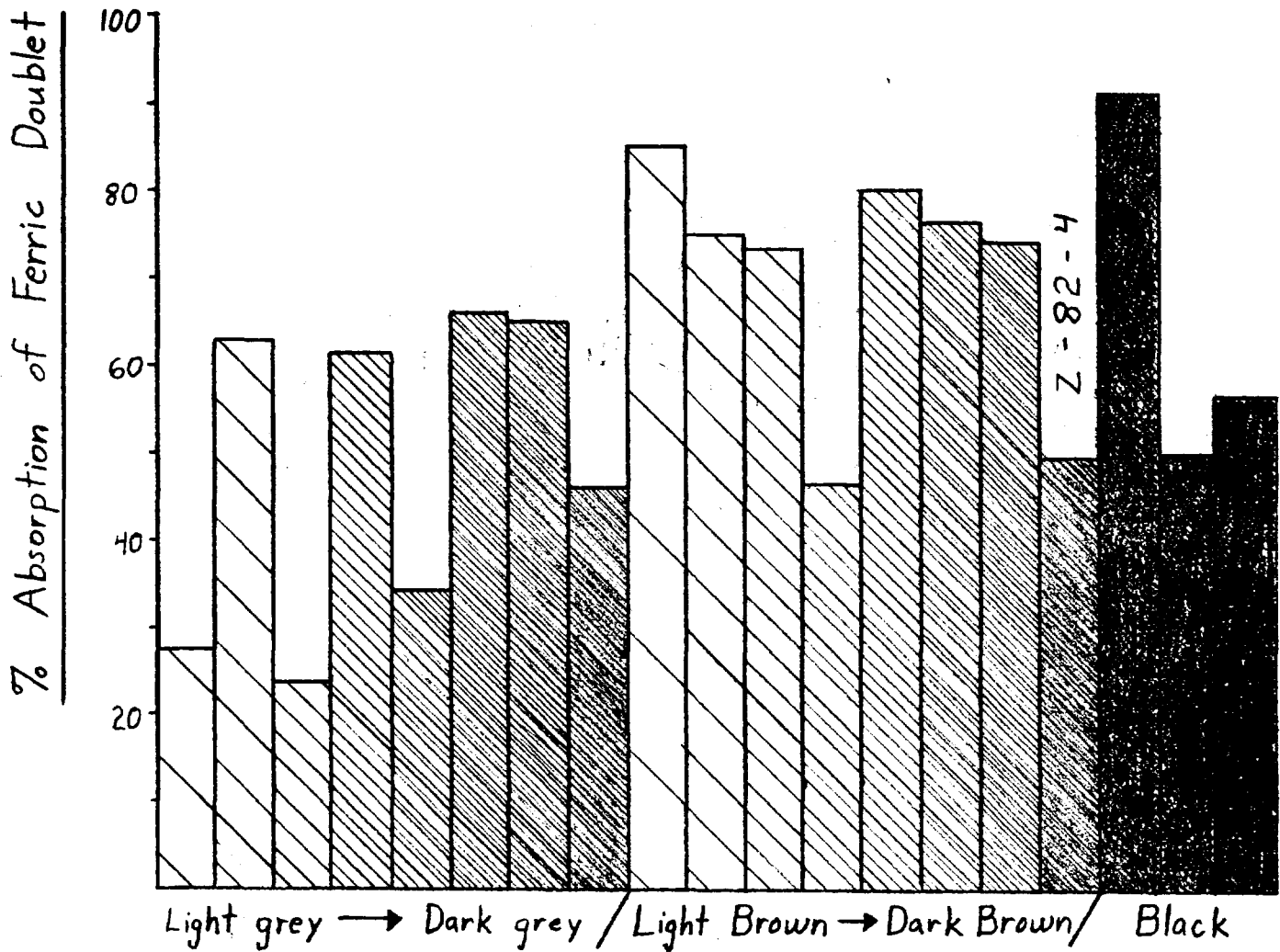
— Ranges Of Quadrupole Doublets and Isomer Shifts



Predominant Doublets ——— •  
 Less Predominant Doublets ——— +

# TABLE 5

Relating the Shale Color to the % of Absorption

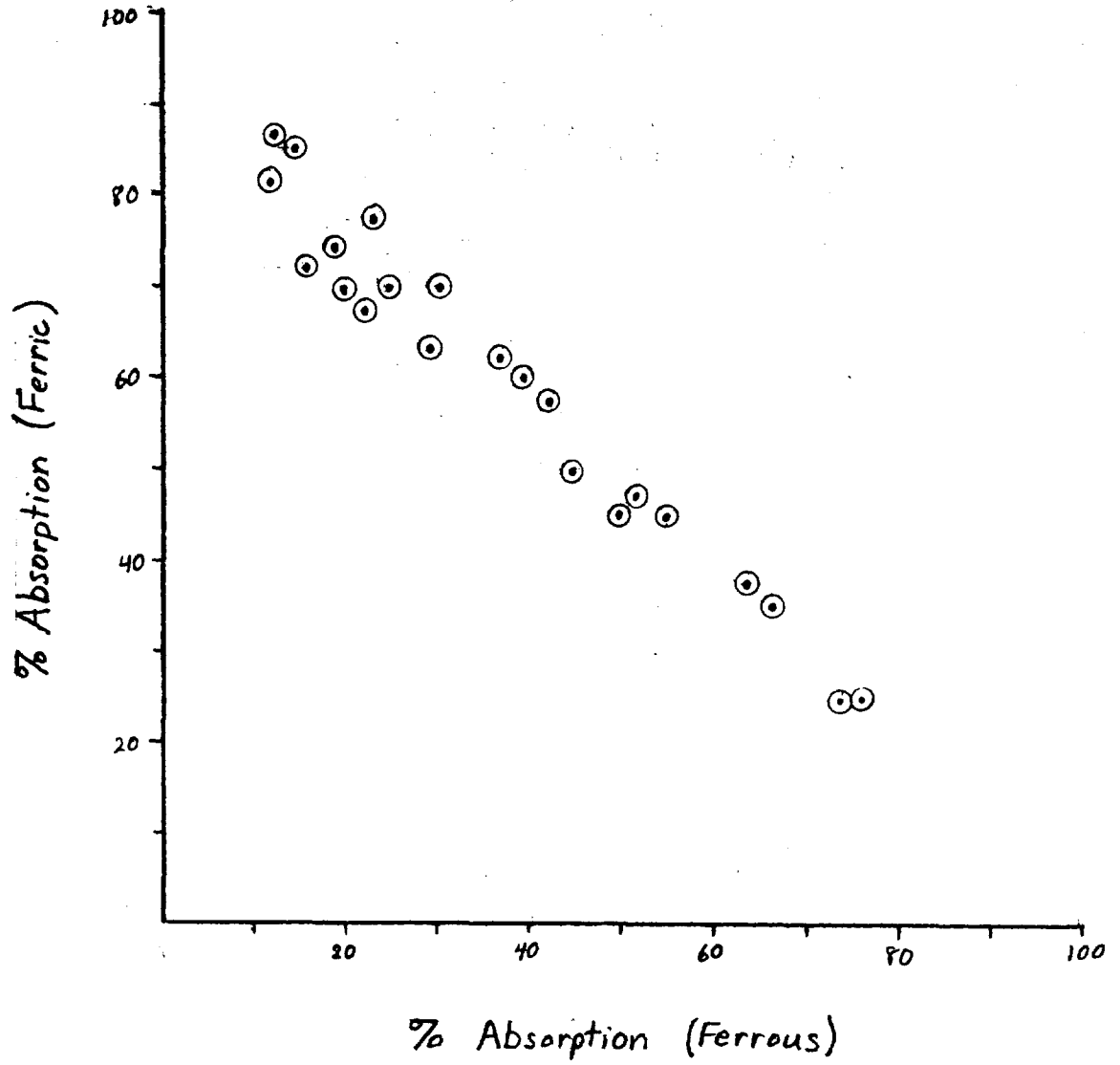


Shale Color (In Order of Increasing Organic Content)



TABLE 6

■ % Absorption (Ferrous) vs. % Absorption (Ferric)



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