

MÖSSBAUER SPECTROSCOPY: PRINCIPLE AND PRACTICE

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ABSTRACT

Mössbauer Spectroscopy has started to come into its own as an analytical tool. In order to understand what has been accomplished and the potential applications of the Mössbauer Effect, one must understand nuclear resonance absorption and how it is effected by the environment of the absorbing nucleus. The perturbation of the nuclear energy levels of Mössbauer nuclides and the resultant characteristics of Mössbauer spectra are reviewed. This includes the isomer shift and its dependence on the electron density about the nucleus, quadrupole splitting and magnetic hyperfine splitting as well as the temperature dependence of these properties. Correlations of the above properties with the ionic state, electronegativity of a bonding component or with theoretical electron density calculations can be accomplished. The Debye-Waller factor for both the source and absorber material places certain restrictions on the ability to observe the Mössbauer Effect with all possible Mössbauer nuclides. Two typical Mössbauer spectrometer systems are described. One utilizes a constant velocity mode of operation for obtaining data, at one velocity at a time. The other utilizes a constant acceleration mode of operation which scans the chosen velocity range repetitively, storing the counting data in a multichannel analyzer. The basic detection system is the same for both systems but the readout devices may differ. Application of Mössbauer Spectroscopy in the study of surface effects such as adsorption and the study of the bonding of some organo metallic compounds will be discussed.

Another technique has been added in the field of spectroscopy. This new method of analysis depends upon the observance of nuclear resonance absorption which in turn depends upon the recoil free emission and recoil free absorption of gamma rays, or the Mössbauer effect. The term Mössbauer Spectroscopy has been applied to this new and very useful instrumental method which complements the more established techniques of NMR, ESR and x-ray diffraction.

The theory behind the Mössbauer effect has been fully described by Mössbauer (23), Frauenfelder (24) and Wertheim (3) and will not be described in detail here. Certain nuclides (Mössbauer nuclides) exhibit a nuclear decay scheme where the transition from the first excited nuclear level (and sometimes second excited nuclear levels) to the ground state may occur with the recoilless emission of a gamma ray. This gamma ray is uniquely capable of raising a similar nucleus in the same type environment from the ground state to the first (or second) excited nuclear level by recoilless absorption (resonant absorption). Most of the elements that have one or more of these Mössbauer nuclides are shown on the accompanying chart (Fig. 1). The resonant absorption process depends on the fact that the emitting (source) and absorbing (sample) species are bound in a crystal lattice.

Resonance absorption may be destroyed by employing the Doppler effect. If we move either source or absorber relative to the other we may alter the conditions

necessary for resonance absorption. Essentially what happens is that by moving either the source or absorber toward the other (a positive Doppler velocity) we increase the energy of the gamma ray as seen by the absorbing species. By moving one away from the other (a negative Doppler velocity) we decrease the energy of the gamma ray as seen by the absorbing species. A complete Mössbauer spectrum would therefore be the plot of the rate of transmission of the gamma ray through the absorbing sample as a function of this Doppler velocity. The resonant condition results in a noticeable decrease in transmission (resonant peak). The parameters of such a spectrum include M (or ξ), the percent decrease in transmission (magnitude of the peak) at the resonant velocity and Γ , the width of the resonant peak at half maximum as shown in Fig. 2.

Resonance absorption occurs at zero velocity only if both the emitting and absorbing species are in the same physical environment. If this is not true then the resonance absorption may occur at a non-zero velocity. This displacement of the resonance from zero velocity is called the chemical or isomer ($I.S. = \delta$) (Fig. 3). The isomer shift value is a linear function of the s electron density and for Fe-57 decreases with increasing s electron density (1). The d electron density affects the isomer shift mostly by shielding the s electron from the nucleus. Adding d electrons to the atom of interest decreases the electronic charge density at the nucleus, an effect just the opposite of that resulting from the addition of s electrons. The contribution to the shift from the p electrons is very small (3).

Since the electron density at the nucleus is a function of the oxidation state of the absorbing atom and of the electronegativity of its nearest neighbors we have a means of qualitatively identifying compounds, determining oxidation states and structural information concerning the absorbing material. For example, in Fig. 4 we can see how different tin (IV) halides give very noticeably different isomer shifts. The SnF_4 gives a quadrupole splitting because of the inhomogeneous field of surrounding F atoms (it is believed to have a polymer like structure).

Quadrupole splitting ($QS = \Delta$ distance between the two resonance peaks) is due to the interaction of the inhomogeneous electric field at the nucleus (due to the environment) with the electric quadrupole moment of the excited nucleus. The result is a doublet or two resonant peaks. This occurs because the first nuclear excited level splits into two sublevels and two transitions (of slightly different energy) may occur (Fig. 5). Quadrupole splitting may be related quantitatively to the oxidation state and the nature of the chemical bonding of the absorbing atom (1). It also may be used as a method of determining the symmetry of crystals and crystal distortion incurred by substitution in the compound as shown in Fig. 6. The isomer shift of a quadrupole split spectrum is taken as the displacement of centroid from zero velocity. In Fig. 6 the isomer shift of the nitroprusside is different than that of the ferrocyanide due to the fact that the s electron density about the iron atom has changed when one of the ligands changed.

Another interaction, that of the nuclear magnetic moments and the external or intermolecular magnetic fields results in magnetic hyperfine splitting (MHS) of the spectra (a nuclear Zeeman effect). (Fig. 7) In the case of iron we may obtain a spectrum with six resonances. Identification of magnetically ordered structures and determination of Curie and Neel temperatures for many materials may be accomplished by studying their MHS spectra (3). The MHS of rare earth intermetallic compounds has been used to determine the magnetic properties and structure of these materials (25).

Double six line spectra may be obtained when the iron present in the absorber may be in either of two different environments (having different nearest neighbors) or two different crystal structures (tetrahedral and octohedral) where the internal magnetic field is different at each site. A composite of a six line and a one or two line spectrum may occur when two forms (magnetic and nonmagnetic) of a material such as Fe_2O_3 are present in the absorber.

The isomer shift for split spectra is recorded by taking the centroid of the spectrum and measuring its displacement from zero velocity.

Mössbauer spectra may not always be as uncomplicated as one of the three basic forms described. But combinations and perturbations of the basic forms can usually be separated into component factions (basic forms) with little difficulty, (especially with computer curve fitting programs) providing a wealth of information about the absorber sample. Generally it may be said that the area under the resonance peak is proportional to the amount of the element under investigation in a particular type of sample (22). Mössbauer Spectroscopy can provide quantitative information as well as qualitative information about the sample.

Examples of some of the information obtained using Mössbauer spectroscopy may be shown with a few typical spectra. We have seen the different isomer shifts of the tin (IV) halide compounds. In most iron compounds a quadrupole splitting is typical, as shown in Fig. 8 (a wide splitting for ferrous and a narrow splitting for ferric compounds).

Many different iron compounds have their isomer shifts and quadrupole splittings listed in a table compiled by Fluck et al. The accompanying diagram (Fig. 10) shows certain band locations on the velocity axis where isomer shift and quadrupole split values may be found. The influence of temperature on these values is generally linear from -120°C to $+80^\circ\text{C}$ (1). The influence of pressure varies according to the crystal structure (22).

Temperature dependence of the electric quadrupole splitting and isomer shift values can provide much information on chemical structure and bonding (26). For example, the sixth electron in excess of the half filled shell in ferrous compounds (d^6) causes a sharp temperature dependence on the quadrupole splitting. At the lower temperature the lowest molecular orbital is most populated and therefore we find the highest quadrupole splitting. As the temperature rises all molecular orbitals are populated equally and ΔE approaches zero. The d^5 configuration for iron has a much smaller temperature dependency. Brady, Duncan and Mok have reported the temperature dependence on a number of high and low spin iron compounds (27).

Pressure dependence of Mössbauer spectra may be much smaller than temperature dependence unless the material can be significantly compressed to alter the bond lengths or the environment of the absorbing nucleus. If all the bonds were symmetric and changed equally with pressure the electron density would change resulting in an isomer shift. Quadrupole splittings may change with pressure if asymmetry is present in the absorber. Mössbauer Spectroscopy may thus detect small asymmetries which are not measurable by x-ray diffraction (28).

Other studies of isomer shifts have been made on iron compounds (13), iron organic compounds (14), tin compounds (2, 15, 16), and iodine compounds (17).

Studies on the bonding of clathrates (Kr) and rare gas compounds (3) have been made using Mössbauer Spectroscopy. Structural data on many compounds such as iron carbonyls, ferrates, dipyrindyl iron complexes and SnF_4 (polymer-like structure) (1, 2) have also been studied using this new non-destructive method of analysis.

Wertheim and co-workers have correlated the isomer shift values of Fe-57 as a function of 3d and 4s electron charge density (13). Their diagram is shown in Fig. 9 and it provides a useful aide in determining electron charge density for compounds of interest.

Since most of the original work in the field of Mössbauer Spectroscopy has been with iron, many potential applications of this technique in the non-destructive testing of metals and alloys have already been discussed (5, 6). Mössbauer Spectroscopy may be used in quality control or for the study of alloy structure and its relation to the magnetic hyperfine fields of the alloy. Corrosion and certain surface defects on metals or gas absorption on metal surfaces (e.g. catalysts) may also be studied using this technique. Mineral assay methods are being developed since certain minority ingredient can usually be detected in a host matrix (2).

Many of the above studies require thick samples which prohibit transmission type experiments. Therefore a scattering technique is used. This requires that both the source and detector be on the same side of the absorber (shielded from one another). The re-emitted radiation (from the decaying resonantly excited absorber nucleus) is detected and instead of a decrease in counting rate at resonance we observe an increase in detection of the Mössbauer gamma ray, resulting in a Mössbauer spectrum just the inverse obtained in a transmission experiment.

Investigation of iron compounds has extended the use of Mössbauer Spectroscopy to the field of biology. Gonzer, Grant and Kregzde (10) have studied hemoglobin and some of their results are shown on Fig. 11. The different spectra result from different ligands bound to the central iron atom. A more extensive study of hemoglobin has recently been published by Lang, et al. Other work has been done with heme and hemin compounds (12) ferredoxin (11) and iron porphyrins (8).

Iodine is another element that has recently allowed Mössbauer Spectroscopy to be used in the biological field.

Cryogenic techniques (to provide a stiff matrix) have been developed that allow the experimenter to study species stable or more easily available in solution. Some of these techniques and the general application of Mössbauer Spectroscopy in Biology were the subject of discussion at a 1965 symposium (9).

The study of other Mössbauer elements is discussed extensively in recent publications (18, 19, 22). A new index of all publications concerning Mössbauer investigations has recently been published (20). This Mössbauer Effect Data Index has the compilation of all the data obtained and lists the parameters by nuclide.

Although many applications have been found using Mössbauer Spectroscopy, the field is just blossoming. Most of the results must be interpreted on an empirical basis. Spectra must be compiled and instruments compared to a standard reference point in order that the values obtained by different investigators be correctly interpreted.

It is interesting to note that the National Bureau of Standards in the United States now offers a standard reference crystal of sodium nitroprusside which gives a sharply defined quadrupole split spectra. The distance between the peaks (in mm/sec.) provides an accurate calibration of the investigator's velocity scale. Dr. J. J. Spijkerman of the NBS Laboratory has authored a recent review article on Mössbauer Spectroscopy which provides a compilation of publications for 1965, categorized by element with comments on the nature of each study, as well as an excellent list of references(22). Another excellent review was recently published by Greenwood in England (26).

It is obvious from the expanding number of publications that the Mössbauer Effect is becoming a more effective analytical technique. The fact that Mössbauer Spectroscopy has been accepted as a member of the spectroscopy family is also obvious from the availability of commercial Mössbauer Effect Spectrometers.

Commercial and homemade Mössbauer Spectrometers may be divided into two basic types, mechanical (usually constant velocity) and electro-mechanical (usually constant acceleration). The mechanical systems are many and include precision lathes, cam devices, pulley arrangements and piston type drives. All of these devices are limited to the relatively low velocities (usually less than 2 cm/sec.) but may be used to study most iron and tin systems. A precision lathe type of Mössbauer Spectrometer that is commercially available (Fig. 12) moves either the source or absorber at a given velocity (between 0.05 and 15 mm/sec.). This instrument employs a synchronous motor, and a ball-disc integrator transmission system to vary the velocity. An o-ring coupling moves the precision machined steel lead screw which in turn moves the source or absorber stage. When operating a constant velocity system, taking data for one velocity at a time, one must be very careful that the detection electronics do not drift or the resultant spectrum will be worthless.

An electromechanical transducer is the type of instrument used for a constant acceleration type of Mössbauer Spectrometer. A voltage signal (triangular, saw-tooth or sinusoidal) is transformed into a velocity in the transducer. Thus the transducer may sweep through a spectrum of velocities (from the maximum in one direction through zero to a maximum in the other directions) during each cycle. A feedback system corrects for any deviation from the reference voltage signal.

When operating at constant velocity the data is accumulated in one or two scalars. A multichannel analyzer operating in the multiscaler mode is required when operating at constant acceleration. Each channel will represent a scalar for a given velocity. Therefore the motion of the transducer must be synchronized to the MCA while it is advancing through its channels. Synchronization is most frequently established by slaving the Mössbauer spectrometer to the MCA by deriving the reference velocity signal from the address register of the MCA.

The National Bureau of Standards system uses the analog signal from the address register to drive the transducer, with a maximum velocity of 20 cm/sec. (commercial units are available up to 60 cm/sec.) (Figs. 13A, B). A constant velocity mode of operation is also included in the NBS system.

The usual detection system used with a Mössbauer Spectrometer would include a detector, a high voltage supply pre-amplifier, a linear amplifier, single channel analyzer scalar and timer. A multichannel analyzer capable of operating in the multiscaler mode should be included if operating in the constant acceleration

mode. This mode of operation is favored because it averages any small electronic drift problems in the detection system. The type of detector chosen depends upon the gamma ray of interest. Gas filled proportional counters are generally used below 40 Kev.

Velocity spectra may be obtained directly from the MCA by using an x-y recorder. Digital data is obtained with a typewriter or paper readout system. This is necessary if you wish to perform a computer analysis of the data.

Cryogenic accessories to cool both source and absorber during Mössbauer experiments are sometimes necessary. Cooling is required in order to measure the Mössbauer effect in systems containing certain nuclides (ones with low Debye temperatures). Many commercially available dewars are designed to contain different cryogenic liquids including helium. Another system available provides cooling by the Joule-Thomson expansion of hydrogen gas. Control of gas pressure allows temperature variation from 16°K to 70°K to better than $\pm 0.5^\circ\text{K}$. In any cryogenic system one must be extremely careful that the unit does not introduce any vibration to the source or absorber or resonance absorption may be destroyed.

Mössbauer sources for many nuclides are also available commercially and may vary in composition. Some may be electroplated (Co-57 on copper, palladium or platinum) or just potted in plastic (Sn-119m as BaSnO₃). Absorbers are easily made by mounting the sample (foil or powder) between two sheets of 5 mil mylar with the help of double backed tape. Cryogenic mounts are usually metallic for better heat conduction properties.

Studies into the bonding of organo metallic compounds (especially organo-tin compounds) have been fairly numerous. Interpretation of isomer shift values and a compilation of different data has been summarized in two papers by Herber et al (29, 30). Fig. 14 shows how the Mössbauer parameters for a number of tin compounds may be grouped. Various organo-tin compounds fall in the crosshatched areas.

A recent investigation into the bonding of iron in coal using Mössbauer Spectroscopy was done by Lefelhocz and Kohman of Carnegie-Mellon University and Friedel of the Bureau of Mines in Pittsburgh (31). Various coal samples were run to study the organically bound iron in the coal. Their preliminary work confirms that the iron sulfide in coal consists mainly of pyrite and indicates that non-pyrite iron is in a high spin iron (II) state having octohedral coordination.

The Mössbauer spectra obtained by Lefelhocz et al. could not be compared directly to any other reported spectra. Some spectra with similar δ and Δ values has led them to believe that the iron may be bound to heterocyclic nitrogen aromatic groups in the coal macerals or possibly in a clay-like silicate mineral or gel.

Another area of usefulness for Mössbauer Spectroscopy is the investigation of catalysts and their functions. Very little has been published on this type of work. NSEC has recently been working with a number of companies in this area. Initial results have shown different Mössbauer patterns for new and used catalysts of iron oxides as well as complex iron compounds. Both magnetic and non-magnetic forms may sometimes be present in different ratios for the new and used catalysts. Hopefully future work will include investigation of these catalysts in working systems to see what influence adsorption (and perhaps reaction) may have on the Mössbauer Spectrum.

Some work has been done on adsorption studies using the Mössbauer effect. Flinn and co-workers studied iron on the surface of Al_2O_3 (32). An anisotropy of thermal vibration relative to the surface was observed. This resulted in unequal peaks in the quadrupole split spectrum. The large quadrupole split also indicated that the iron was present in a highly asymmetric electrical field. The amplitude of vibration was greatest along the axis of the electric field gradient (normal to the surface) compared to that parallel to the surface.

Other adsorption studies have been made by Burton, Goodwin and Frauenfelder at the University of Illinois (33) and by Shpinel and co-workers in Russia (34) and others (35, 36, 37). Comparisons were made between atoms in the bulk of the matrix, in the surface of the matrix and on the surface of the matrix. Variations of the resultant spectra with temperature for each type sample were used to explain the surface dynamics of an atom. It is hoped that Mössbauer Spectroscopy will prove more useful in the study of the surface dynamics, chemical states and magnetic properties of adsorbed particles (including very thin films).

This explanation of Mössbauer Spectroscopy, description of equipment available and the examples of the applications that have been given are all too brief. Much new information concerning the elements we are able to study has been obtained using this very sensitive analytical technique. Some of this information can be obtained by no other method. Other information compliments what has been obtained using NMR, ESR and x-ray diffraction and other analytical techniques. Therefore, we can look forward to increased references to data obtained from Mössbauer spectra and further refinement of Mössbauer Spectroscopy.

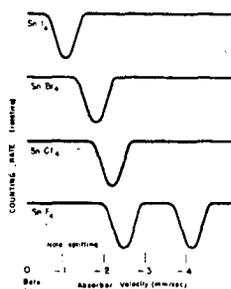


Fig. 4. Mössbauer spectra can contain more than one line, if energy levels are split by interaction that depends on nuclear orientation. In this case SnF_4 spectrum is doublet because Sn^{119} electric moment interacts with inhomogeneous field of surrounding F atoms. (2)

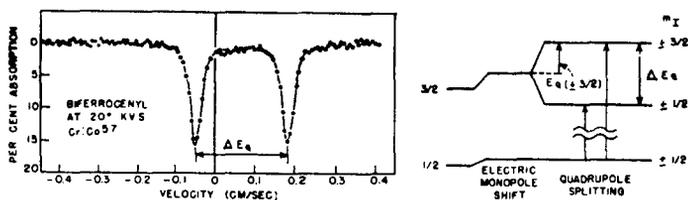


Fig. 5. Quadrupole splitting. The interaction of the nuclear quadrupole moment, Q , with the gradient of the electric field, e_q , is illustrated for nuclear ground-state spin $I_{gd} = 1/2$ and for isomeric-state spin $I_{is} = 3/2$; the diagrams are applicable to Fe^{57} , Sn^{119} , and Tm^{181} , among other isotopes. For the ground state, or any state with $I = 1/2$, Q is inherently zero. An example of a pure quadrupole Mössbauer absorption spectrum is shown. (1)

$$\Delta E_q = \frac{eqQ}{2}$$

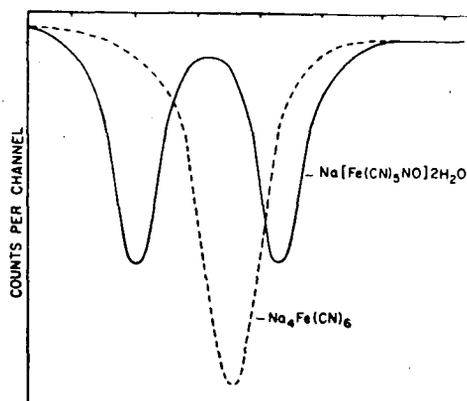


Fig. 6. Mössbauer spectra of an octahedrally symmetric complex $[\text{Na}_4\text{Fe}(\text{CN})_6]$ and of a distorted octahedral complex $[\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}]$, showing the effect of a non-vanishing electric field gradient at the Mössbauer lattice point. (4)

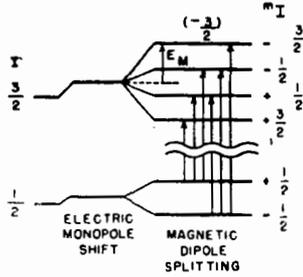
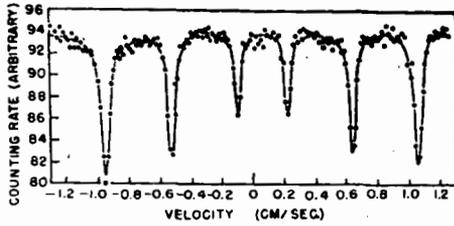


Fig. 7. Magnetic hyperfine splitting for $J_{gr} = 1/2$, $J_{is} = 3/2$. As a result of the selection rule, $\Delta m = 0, \pm 1$, only six of the possible eight lines are observed. The graph shows the Fe^{3+} hyperfine splitting of FeF_3 , which corresponds to a field of 620,000 oersteds. (7)

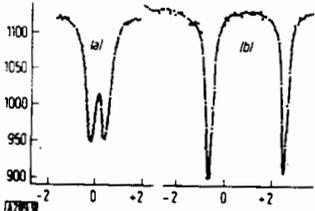


Fig. 8. Mössbauer spectra (a) of $FePO_4 \cdot 4H_2O$ and (b) of $FeSO_4 \cdot 7H_2O$ (11)
 Ordinate: transmission [arbitrary units]
 Abscissa: velocity of the source relative to the absorber [mm/sec]

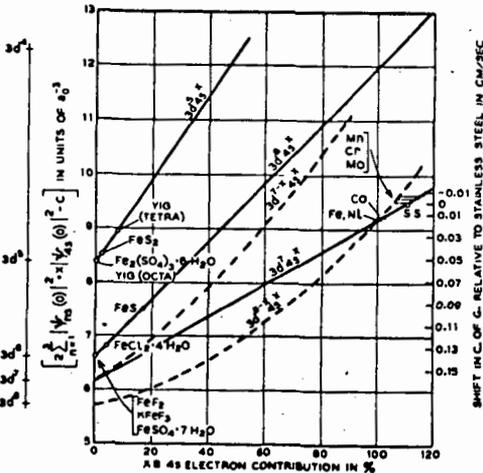


Fig. 9. A possible interpretation of the Fe^{57} Mössbauer isomer shifts in various solids. The total s -electron density is plotted as a function of the percentage of $4s$ character for various d -electron configurations. The reasons for placing the experimental data on given theoretical curves are discussed in the text. The constant $C = 11873 a_0^{-3}$. (13)

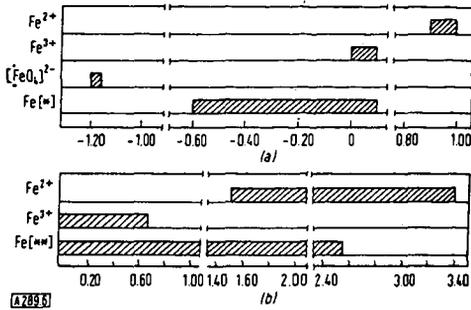


Fig. 10. (a) Values for the isomeric shifts and (b) values for the quadrupole splittings of Mössbauer lines in ferrous and ferric compounds. (s)
 Radiation source: ⁵⁷Co in platinum at 25°C.
 Abscissa: Velocity of the source relative to the absorber [mm/sec].
 Fe [*] = iron in complexes and metals.
 Fe [**] = iron in complexes.

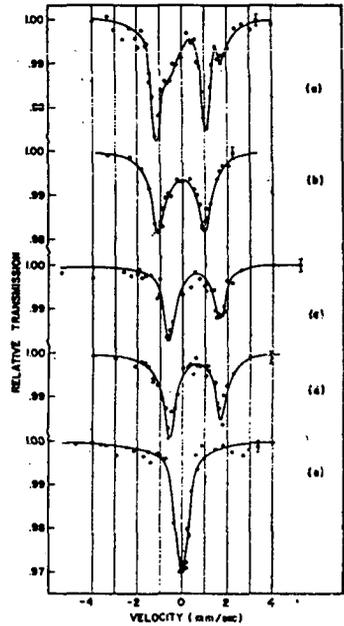


Fig. 11. Mössbauer absorption spectra with a source of Co⁵⁷ diffused into Pt and kept at room temperature and absorbers of (a) rat red cells at 4°K and isotopically enriched with Fe⁵⁷, (b) crystalline rat oxyhemoglobin at 77°K, (c) human CO₂-hemoglobin (in a CO₂ atmosphere) at 77°K, (d) human hemoglobin (in a N₂ atmosphere) at 77°K, and (e) human CO-hemoglobin (in a CO atmosphere) at 77°K. We have used the standard notation that source approaching absorber is positive velocity. (10)

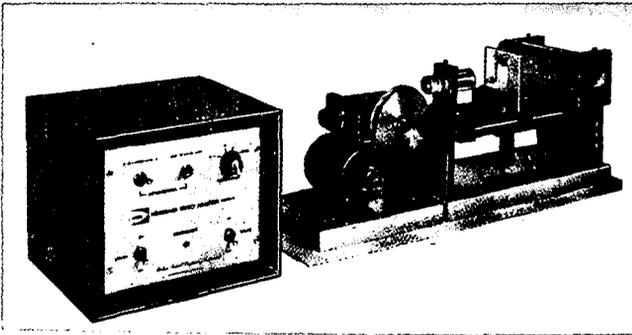


Fig. 12. A Constant Velocity Mössbauer Effect Analyzer

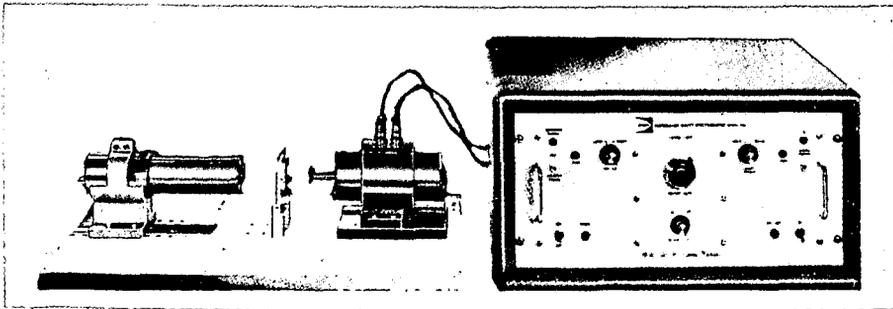


Fig. 13. A Constant Acceleration Mössbauer Effect Spectrometer

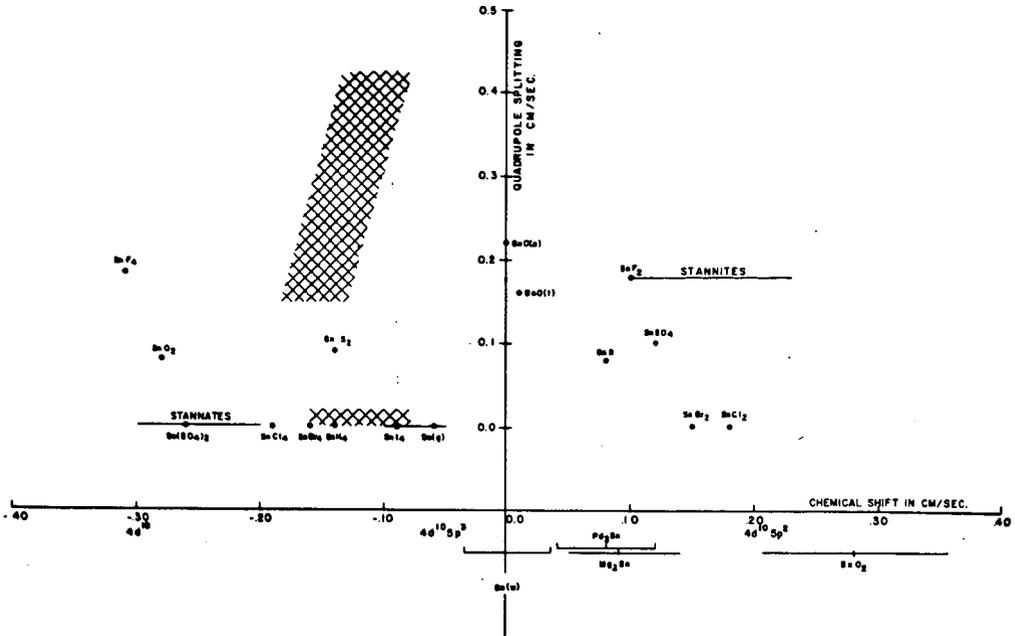


Fig. 14. Correlation diagram of the quadrupole splitting and chemical shift values for Tin Compounds at 78°K (38)

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