Design and performance of a Mössbauer resonance counter

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Publication date:
1974

Document Version
Publisher's PDF, also known as Version of record

Risö-M - 1695

Risö-M - 1695

Danish Atomic Energy Commission

Research Establishment Risö

CHEMISTRY DEPARTMENT

Design and Performance of a
Mössbauer Resonance Counter

by

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March 1974

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Date

Department or group

Chemistry

Group's own registration number(s)

16 pages + 0 tables + 5 illustrations

Abstract

The report describes the design of a resonance counter for Mössbauer studies with iron-57. Various applications in 'beam experiments', 'source experiments', and surface studies are discussed.

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Fi 25-204

INIS Descriptors:

COUNTING TECHNIQUES
FLOW COUNTERS
IRON 57
MOESSBAUER SPECTROMETERS
RESONANCE SCATTERING

ISBN 87 550 0249 8

CONTENTS

1. INTRODUCTION

Most Mössbauer experiments are based on a transmission geometry: an absorber is placed between a source and a counter; either the source or the absorber is moved, and resonance absorption is observed as a decrease in count rate. However, in some cases it may be more favourable to use a scattering geometry, where the absorption is observed via the de-excitation of the absorbing nuclei [e.g. 1, 2]. Mössbauer transitions are normally partly converted, and it is thus possible to detect either the emission of γ-quanta or the emission of conversion electrons, Auger electrons, and X-rays. The electrons, however, have such a low energy (typically 1-10 keV) that they cannot penetrate a detector window; therefore the absorber must be placed inside the detector volume. It is possible to incorporate Mössbauer isotopes in a scintillator [3], but normally a gas-filled counter is used; such a combined absorber-detector is generally called a resonance counter.

Counters for ^{57}Fe based on this principle have been described by i.a. Spijkerman [e.g. 4]; a counter for ^{119}Sn has been described by Mitrofanov et al. [5] and for ^{125}Te by Lebedev et al. [6]. In the ^{125}Te case the energy of the conversion electrons is only about 1 keV, and it is more favourable to detect the accompanying X-rays. More elaborate set-ups, where the electrons are detected with a small β-spectrometer, have been described for ^{119}Sn by Bonchev et al. [7] and for ^{182}W by Kankeleit [8].

Resonance counters can be used in two ways. If the source and the absorber in the counter are of the same material, the maximum resonance is observed when source and counter are stationary, then the Mössbauer spectrum of another moving absorber between the source and the counter can be measured. If, on the other hand, the source and the absorber in the counter are of different materials, either the source or the counter must be moved; then the Mössbauer spectrum of the source can be investigated if the absorber is known or vice versa. Only measurements of the latter type are discussed in the following; here resonance counters have three attractive properties:

1) The sensitivity of the detector for γ-radiation can be made very low; therefore a large resonance to background ratio can be obtained. Typically the ratio is about ten times larger than in a corresponding transmission measurement. This is a potential advantage in 'beam experiments' (cf. sect. 5.1).

2) The electrons have a very short range; for 7.3 keV electrons from ^{57}Fe in metallic iron the attenuation coefficient, μ_K, is thus about $5 \cdot 10^{-5}$ cm^{-1} [9], corresponding to a range of the order of 1000 Å. Therefore only absorption in a thin surface layer of the absorber is registered. This may be exploited in e.g. corrosion studies (cf. sect. 5.3). In principle it should even be possible to distinguish electrons originating at different depths in the absorber and thus to record Mössbauer spectra of successive surface layers. Such measurements, however, are complicated by the emission of L-shell Auger electrons which follow the conversion electrons with a probability of 0.7. A theoretical analysis of the problem has been presented by Krakowski and Miller [9].

3) A resonance counter has a better energy resolution for Mössbauer absorption than a conventional absorber-counter combination, since thickness broadening is negligible. This is a potential advantage in 'source experiments' (cf. sect. 5.2).

The advantages are set off by two drawbacks: A low efficiency - typically only about 10% of that of a conventional system [10] - and a low pulse height resolution (cf. fig. 3).

The present report describes the construction of a resonance counter for ^{57}Fe and summarizes the experiences obtained in various experiments. Some of the results have been published elsewhere - others are purely informative.

2. MÖSSBAUER TECHNIQUE

All Mössbauer spectra were recorded on spectrometers of the

constant acceleration type with transducers made from two Hi-Fi loudspeakers. In the first experiments the velocity drive [11] was operated in pulse height mode; later a drive operating in time mode was used [12]. Since a resonance counter has a low background, a drift in the base line is not serious, and the choice of drive mode is not critical.

The counter (cf. sect. 3) was followed by conventional electronics (Nuclear Enterprise) consisting of preamplifier, amplifier, single-channel analyser, and high-voltage unit. The pulses were stored in a multichannel analyser (Nuclear Data) which was slightly modified [12] to give a reference signal for the velocity drive.

The accumulated data were treated with a 'least-squares method'-computer program [13], which fitted Lorentzian lines to the experimental points. Any set of parameters or linear combinations of parameters could be constrained; normally pairs of lines were assumed to have equal intensity and widths. The velocity calibration was made with the spectrum of an enriched iron foil.

3. CONSTRUCTION OF THE COUNTER

The construction of the counter has been shortly described previously [10], and it is shown in detail in fig. 1. It is a flat, cylindrical flow counter with entrance and exit windows which also serve as cathode, made of 0.5 mm beryllium discs (Bruch Beryllium Co.). On the exit window is glued a 1.5" diameter foil of 310 stainless steel containing 1 mg $^{57}Fe/cm^2$; the actual absorber thickness is about 2 mg/cm^2 (NENC). A rim of conducting paint on the edge of the absorber provides electrical contact with the window. The windows are glued with araldite to aluminium flanges; these are placed on either side of a Lucite flange which supports a number of anode wires of 0.1 mm stainless-steel wire. The Lucite flange also holds inlet and outlet tubes, made of aluminium, for the counting gas.

One, three, and five anode wires have been used and counter thicknesses between 3 and 10 mm were tried. Helium mixed with 1-10% methane was used as counting gas with a flow rate of about

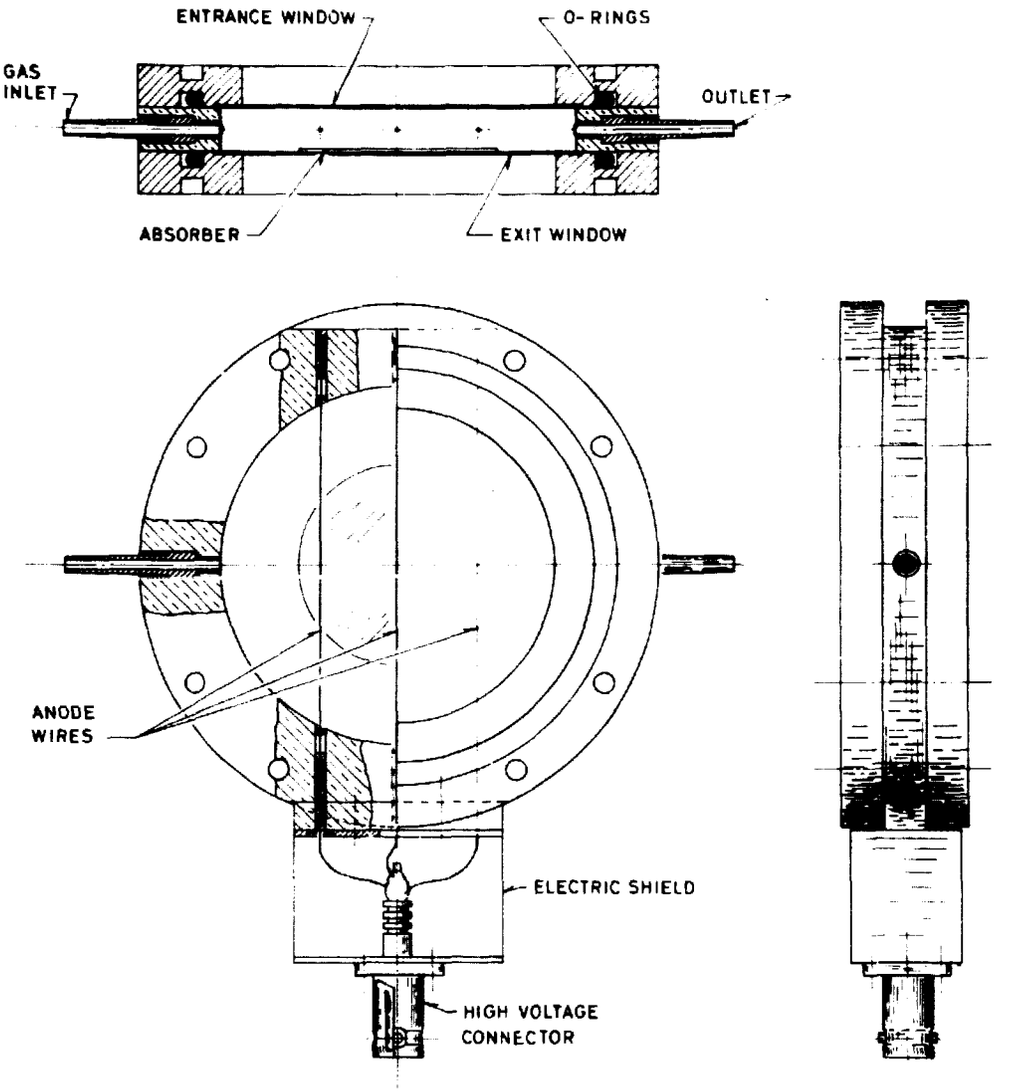

Fig. 1. The resonance counter in the final version for source and beam experiments. Outer diameter 10 cm (Scale 1:1.33).

4 cc/min.

In 'beam and source experiments' the counter was screwed directly on a 30 mm$^{\emptyset}$ collimator with a graded Compton electron shield (cf. fig. 2 in ref. 12). In surface studies the exit window can be replaced by a flat sample (cf. fig. 1 in ref. 14).

4. DETERMINATION OF WORKING CONDITIONS

When the counter is used, radiation from the Mössbauer source goes through the entrance window, passes the volume of counting gas, and is eventually absorbed in the absorber; unabsorbed radiation disappears through the exit window. Conversion and Auger electrons, which are emitted in the backward direction and from not too deep in the absorber, enter the counting volume and must be detected to show resonance absorption. Therefore the counter must have a low detection efficiency for γ-quanta combined with a high efficiency for electrons. To achieve this, we can adjust three parameters: the composition, and in principle the pressure of the counting gas, the thickness of the counter, and the electric field gradient. In addition it is of course possible to select the pulses from the detector by a conventional single-channel analyser.

As a measure of the performance of the counter we determined the count rates when the counter was exposed to a Pd(^{57}Co)-source in movement and at rest. The Mössbauer spectrum of the Pd(^{57}Co)-source is shown in fig. 2, and it is seen that the absorption is measurable at zero velocity. With a large velocity scan, the response to a moving source is nearly equivalent to the background, and the response to a source at rest indicates the background plus a fraction of the peak height.

In a counting gas at 1 atm. composed mainly of helium 7.3 keV electrons deposit their kinetic energy within 1 cm; after a few preliminary experiments we chose a counter thickness of 8 mm. This thickness should allow an almost 100% detection of conversion electrons which enter the counter volume; at the same time the efficiency for relevant γ-quanta should be negligible [15, 16]. Any background registered must therefore be due to Compton electrons produced by γ-quanta in the entrance and exit windows,

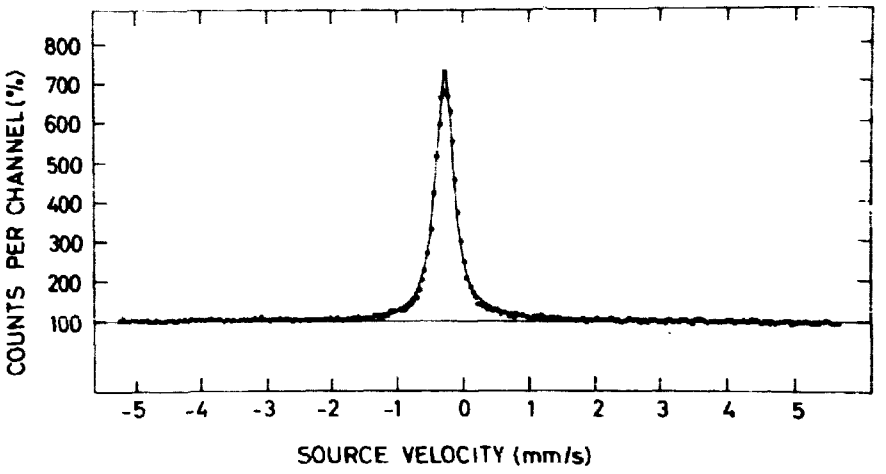

Fig. 2. The Mössbauer Spectrum of a Pd(^{57}Co) Source measured with the resonance counter; the absolute velocity is indicated.

in the absorber, or possibly in the anode wires.

Various experiments with different numbers of anode wires indicated that for the given absorber diameter (∿ 4 cm) three wires were sufficient. The helium-methane ratio in the counting gas was not critical, but the best results were obtained with a mixture of 94% He and 6% CH_4 [10].

The shape of the pulse height spectrum depends upon the high voltage, and the best resolution is obtained in the region 1300-1400 V. Fig. 3 shows the spectra of a source at rest and in rapid movement; the difference between the two spectra represents to a good approximation the energy spectrum of the detected electrons. In recording of Mössbauer spectra the channel analyser was used in 'integral' with a lower discriminator setting corresponding to channel 20 in fig. 3. The ratio between the integrated count rates for the source at rest and in movement is about 2.5:1; this is seen to be in agreement with the Mössbauer spectrum of Pd(^{57}Co) shown in fig. 2.

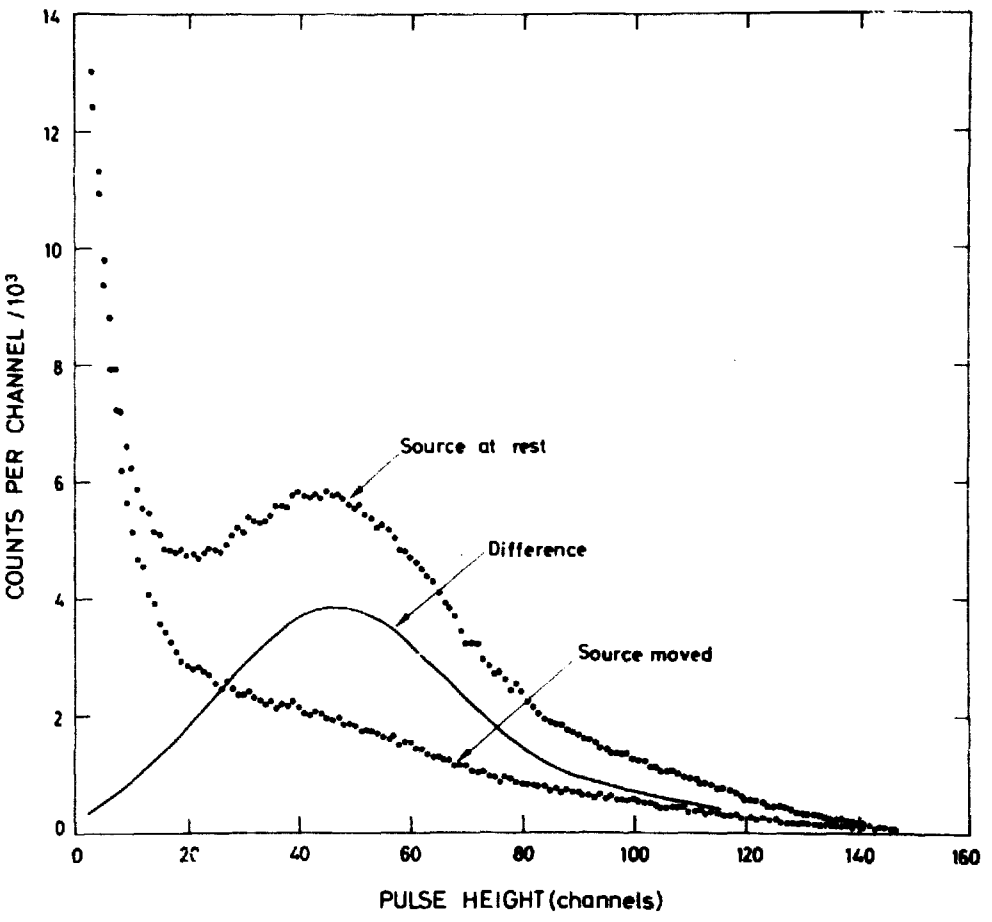

Fig. 3. Typical pulse height spectra from the resonance counter. High voltage 1375 V. 20 μC Pd(^{57}Co) source at 12 cm distance. Live time 4 min.

Alternatively the counter can be operated with a fixed lower discriminator setting, and at various high voltages. Again a difference between the count rates for the source at rest and in movement shows the contribution from conversion electrons, which allows a choice of a suitable high voltage [10].

The two methods of obtaining a good combination of high voltage and discriminator setting yield the same signal to background ratio; this is roughly about twice that normally reported in the literature for such counters.

A direct evaluation of the performance of a resonance counter relative to that of a conventional counter is difficult, i.a. because the geometries, in the nature of things, are different. However, if we define a figure of merit as the ratio between the peak height of a particular resonance and the standard deviation of the counts registered per channel, we can compare spectra recorded for the same time with different techniques.

5. APPLICATIONS

5.1. Beam Experiments

Some Mössbauer isotopes are difficult (or impossible) to form in the excited state by a nuclear decay, whereas it may be achieved in an induced nuclear reaction. In other cases one may want to study the chemical effects of an induced nuclear reaction by Mössbauer spectroscopy. This may lead to the set-up of a Mössbauer beam experiment.

A beam of particles (e.g. thermal neutrons) hits a tilted target and induces the nuclear reactions. The target serves as a source in a Mössbauer experiment which - in order to reduce the background - is performed with the axis forming a right angle with the beam. In experiments based on (n,γ)-reactions the sequence of events is the following: A neutron is absorbed in a nucleus, and capture-γ quanta are emitted in a cascade which with a certain probability passes the Mössbauer level. Since the stopping time of recoil atoms is much shorter than the lifetime of Mössbauer levels, the atom will recoil out of its lattice site and again come to rest before the Mössbauer quantum is emitted. A measurement of 'Mössbauer parameters' (isomer shift etc.) might therefore yield information on the chemical form and (or) the surroundings in which the recoil atom is stopped.

In experiments of this type, the background is much higher and the overall count rate generally lower than in conventional Mössbauer experiments; therefore various special counting techniques have been tried.

We have used the resonance counter and compared it with a proportional counter in studies of the chemical effects of $^{56}Fe(n,\gamma)^{57}Fe$-reactions in $FeC_2O_4 \cdot 2H_2O$ and $K_4Fe(CN)_6 \cdot 3H_2O$, which were irradiated in a thermal neutron beam at the Danish reactor DR 2 [12]. The resonances were very weak and could only be found by computer analysis of the experimental data; therefore it was an advantage that the resonance counter gives spectra with peaks, whereas the proportional counter gives dips; the idea that the observed resonances were an artefact of a curved base line could then be excluded. Further the resonance counter offered a direct comparison with results obtained in studies of $^{57}Co(EC)^{57}Fe$-reactions (cf. sect. 5.2). On the other hand, because of the poor energy resolution of the resonance counter, its 'figure of merit' (cf. sect. 4) was not better than that of the proportional counter.

An avalanche counter, also based on detection of conversion electrons, has been described by J. Christiansen et al. [17] and used by them in studies on the $^{56}Fe(d,p)^{57}Fe$-reaction. Such a counter has no energy resolution, but its time resolution is of the order of some nsec; this permits a time-gating technique which, combined with a pulsed beam, allows an efficient suppression of the background. Since the resonance counter works in the proportional region, its time resolution is modest, and it is not suited for coincidence measurements. In any case, it would hardly be a feasible solution for neutron beam experiments.

5.2. Source Experiments

Mössbauer spectroscopy is well suited for studies of chemical effects of nuclear decay in solids. The $^{57}Co(EC)^{57}Fe$-decay has naturally received most attention, and typically ^{57}Co-labelled cobalt compounds or ^{57}Co-doped iron compounds are used as Mössbauer sources and measured in a conventional transmission geometry. The emission spectra of such sources are complex and normally the resonance lines are weaker and considerably broader than in corresponding absorber spectra. The mechanisms behind these effects are not fully understood, but it is reasonable to assume that they are related to a radiolysis or radiation damage of the crystal lattice.

We have on various occasion [e.g. 18] attempted to use the resonance counter in order to improve the resolution of source spectra, and an example ($Mn_3[^{57}Co(CN)_6]_2.12H_2O$) is shown in fig. 4. A large 'signal to background' ratio is observed, but the 'figure of merit' (cf. sect. 4) is not better than can be obtained with a conventionel technique. A comparison between spectra of $Fe(^{57}Co)C_2O_4.2H_2O$ recorded with the resonance counter and a scintillation counter is shown in fig. 3 of ref. 10.

The line width of a recorded resonance is roughly the sum of the linewidths of the source and absorber; therefore a reasonable improvement in the resolution of source spectra can only be obtained if the source linewidth is not too large. For the Fe^{2+}-resonances in $Fe(^{57}Co)C_2O_4.2H_2O$ with a linewidth of about 0.4 mm s^{-1}, the resonance counter gives lines which are significantly more narrow than observed with a conventional counter [10,12]. For the $Fe(CN)_5^{2-}$- resonances in cobaltihexacyanides with a width of about 1 mm s^{-1}, on the other hand, the improvement was found to be negligible [18].

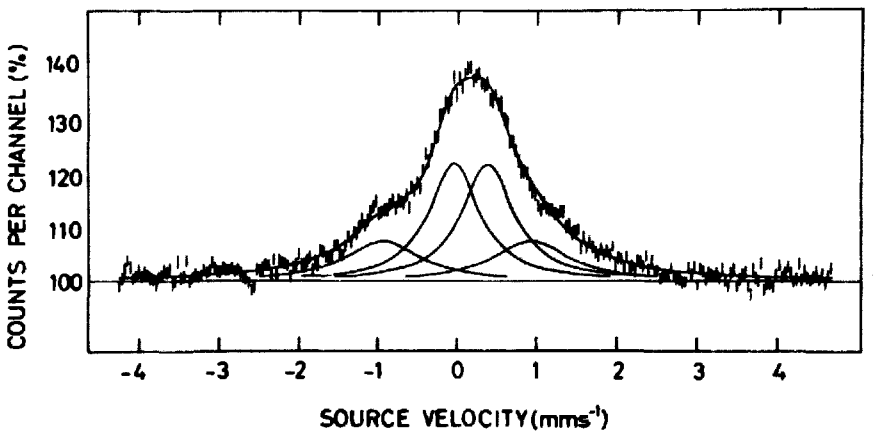

Fig. 4. Mössbauer emission spectra of $Mn_3[^{57}Co(CN)_6]_2.12H_2O$ recorded with the resonance detector. Reference velocity: Metallic iron.

5.3. Studies of Conducting Surfaces

As described in ref. 14 the resonance counter can be used for surface studies by replacing the flange with the exit window at the stainless-steel absorber by a sufficiently flat sample. Since the sample then forms part of the cathode, its surface must be conducting or at least be a thin layer on a conducting material.

We have made preliminary measurements of surfaces of pure iron and various corroded iron plates. A typical example [14] is shown in fig. 5. The spectrum was recorded with a 5 mm iron plate covered with a thick layer of rust, and it exhibited a single narrow doublet with an isomer shift of 0.40±0.03 mm s^{-1} relative to iron and a quadrupole splitting of 0.55±0.02 mm s^{-1}. These values show that the rust is essentially composed of γ-FeOOH. A similar doublet (Δ = 0.69 mm s^{-1}) has been observed by Terrell and Spijkerman [19] with an X-ray scattering technique and was ascribed to β-FeOOH. Since the X-rays have a higher penetration power than conversion electrons, spectra recorded by means of X-ray scattering represent a thicker surface layer; therefore the difference in spectra may be ascribed to a varying structure of the surface with depth.

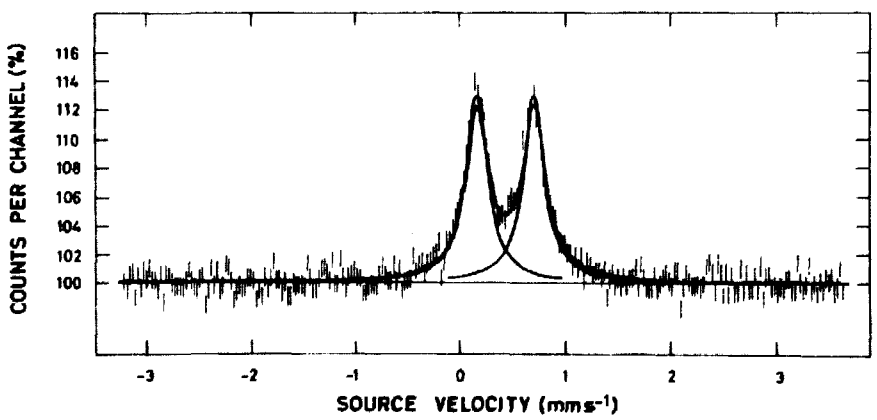

Fig. 5. Mössbauer spectrum of a rusty 5 mm iron plate, substituted for the exit window in the resonance counter. Source: Pd(^{57}Co). Reference velocity: Metallic iron. [14] .

We attempted to study the surfaces of some polished geological samples (kindly supplied by The Mineralogical Museum, University of Copenhagen), but with discouraging results. Thus, the spectrum of a sample of basalt, containing so much metallic iron that is was electrically conducting, on the whole only showed the presence of Fe_2O_3 and Fe_3O_4. Apparently the preparation of the surface had led to an oxidation.

5.4. Studies of Insulating Surfaces

We have only made a few surveying experiments with different techniques for measurements of insulating surfaces.

Sufficiently small flat samples can be placed directly on the exit window, replacing the stainless-steel absorber; at the same time the collimator opening must be reduced correspondingly. A reasonable spectrum was obtained from a single crystal (10 x 10 x 1 mm) of $K_4Fe(CN)_6.3H_2O$.

Polished samples can in principle be covered with a thin layer of aluminium by evaporation. In practice, however, it seems impossible to obtain sufficient conductivity without preventing the conversion electrons from entering the counter.

6. CONCLUSION

A Mössbauer resonance counter gives spectra with a much higher peak-height to background ratio than a conventional absorber-counter combination; further, the line broadening in the absorber due to thickness effects, is negligible. Therefore it was reasonable to expect that a resonance counter could be used with advantage in source and beam experiments. In the actual experiments, however, it appeared that the advantages were largely set off by a much lower sensitivity.

Applications in studies of thin layers and surfaces are more promising; and it is noteworthy that the only systematic studies with a resonance counter [e.g. 20] have been within this field. Here Mössbauer measurements may supplement measurements by various types of electron spectroscopy [e.g. 21,22], which give related information [23] for surface layers only a few atomic distances thick.

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ISBN 87 550 0249 8