

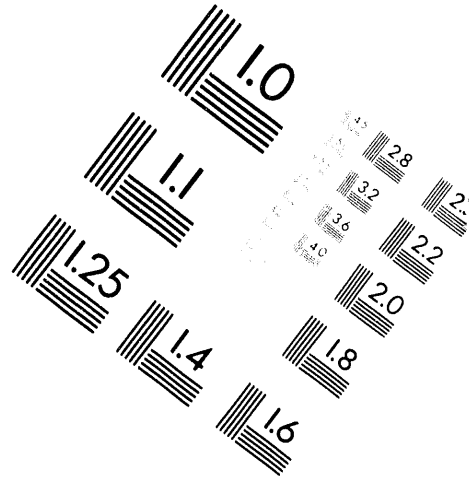
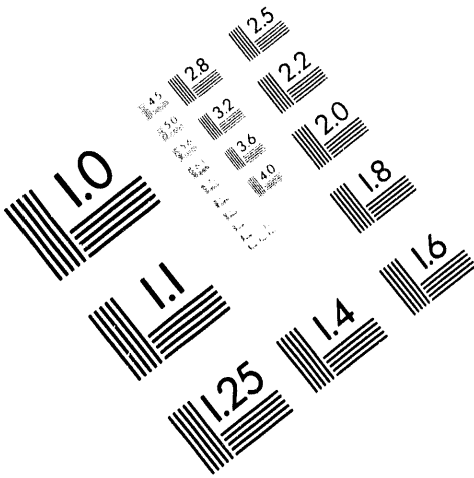


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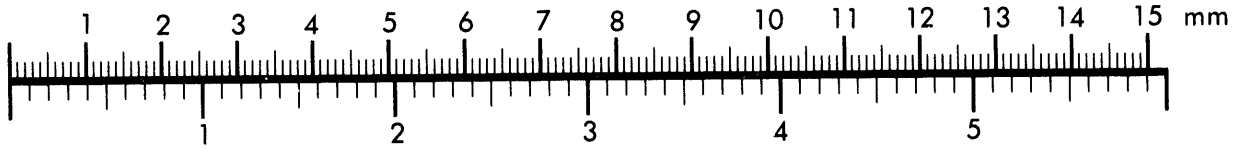
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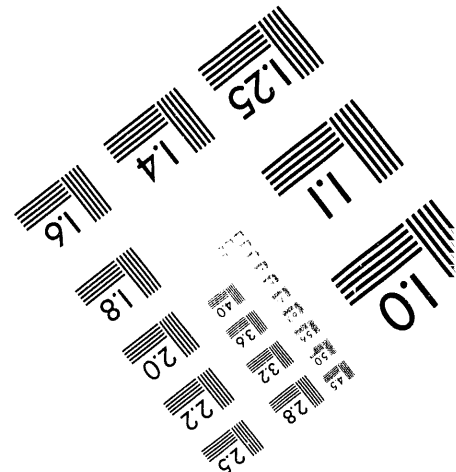
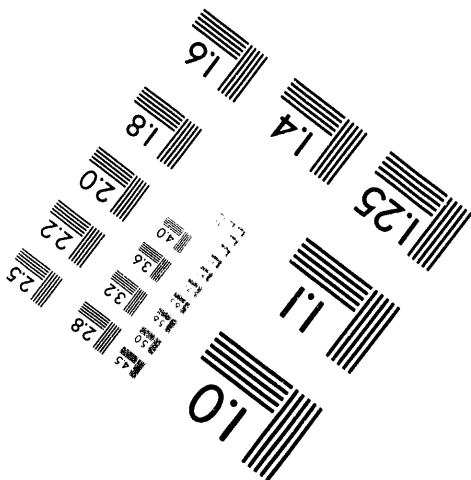
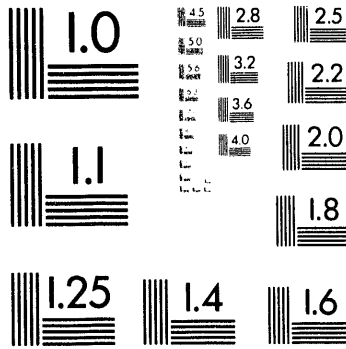
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**SYNCHROTRON MOSSBAUER SPECTROSCOPY OF POWDER SAMPLES (\*)**

E. E. Alp, W. Sturhahn, and T. Toellner.

Advanced Photon Source, Argonne National Laboratory,  
Argonne, Illinois 60439, USA

**ABSTRACT**

Synchrotron Mossbauer Spectroscopy, SMS, is an emerging technique that allows fast and accurate determination of hyperfine field parameters similar to conventional Mossbauer spectroscopy with radioactive sources. This new technique, however, is qualitatively different from Mossbauer spectroscopy in terms of equipment, methodology, and analysis to warrant a new name. In this paper, we report on isomer shift and quadrupole splitting measurements of Mohr's salt,  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  for demonstration purposes. Theoretical calculations were performed and compared to experiments both in energy and time domain to demonstrate the influence of thickness distribution and preferential alignment of powder samples. Such measurements may prove to be useful when the data collection times are reduced to few seconds in the third generation, undulator based synchrotron radiation sources.

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Synchrotron Mossbauer Spectroscopy, SMS, is an emerging technique that allows fast and accurate determination of hyperfine field parameters similar to conventional Mossbauer spectroscopy with radioactive sources. This new technique, however, is qualitatively different from Mossbauer spectroscopy in terms of equipment, methodology, and analysis to warrant a new name. In this paper, we report on isomer shift and quadrupole splitting measurements of Mohr's salt,  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  for demonstration purposes. Theoretical calculations were performed and compared to experiments both in energy and time domain to demonstrate the influence of thickness distribution and preferential alignment of powder samples. Such measurements may prove to be useful when the data collection times are reduced to few seconds in the third generation, undulator based synchrotron radiation sources.

### INTRODUCTION

Scattering of synchrotron radiation from Mossbauer nuclei<sup>(1)</sup> in the forward scattering geometry<sup>(2)</sup> allows measurements of hyperfine interaction parameters similar to conventional Mossbauer spectroscopy with radioactive sources. This time domain spectroscopy, however, has its own subtleties in terms of coherent speed up of forward scattered radiation<sup>(3,4)</sup>, as well as its own instrumentation and analysis techniques. Therefore, we will refer the use of this technique for conventional spectroscopy purpose of hyperfine field determination as "SYNCHROTRON MOSSBAUER SPECTROSCOPY, SMS". Some of these subtle aspects are well understood for samples with uniform thickness. However, thickness distribution, and preferential alignment of grains in powder samples leads to complications in data analysis. In this paper, we report on isomer shift and quadrupole splitting measurements of Mohr's salt,  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ . Calculations are performed both in energy and time domain to demonstrate the level of understanding for nuclear forward scattering method, as well as to study the effect of thickness distribution and preferential alignment of powder samples. The main purpose of the study is to assess and demonstrate the potential of this new technique, point out the difficulties, and motivate the development of new crystal optics to reduce the data collection time to few seconds at the third generation synchrotron radiation sources with dedicated beamlines like the ESRF (France), the APS (USA) and the SPring-8 (Japan).

## EXPERIMENTAL SETUP

The time domain Mossbauer spectroscopy using synchrotron radiation in the forward scattering geometry requires special optics and detectors. Our set-up, shown in Figure 1, involves a high heat load monochromator as first optical component. This is followed by a novel, nested, 4-bounce Si crystal monochromator which provides 5 meV (FWHM) bandpass at 14413 eV, and an avalanche photodiode detector connected to fast timing electronics. The experiments were carried at the 24 pole Wiggler beamline F-2 at CHESS of Cornell University.

The first monochromator used in this experiment was Si (111) double crystal, fixed exit monochromator, where the first crystal is water cooled via In-Ga liquid alloy providing the thermal contact between the first crystal and its the copper base. The intrinsic angular acceptance of Si (111) at 14.413 keV is 18  $\mu$ rad, corresponding to a calculated energy bandpass of 1.9 eV. We had measured an energy bandpass of 4 eV.

The second optical component is the high energy resolution monochromator. This monochromator consists of two channel-cut Si crystals, in a nested geometry (5,6). The outer crystal is a Si (4 2 2) channel-cut with an asymmetric cut of  $-20^\circ$  for Bragg angle of  $22.83^\circ$  with an angular acceptance of 27  $\mu$ rad. The second crystal which is placed inside is a Si (10 6 4) channel-cut reduces the energy bandpass to 5 meV (FWHM). This bandpass has been measured by rocking the Si (10 6 4) channel cut with respect to Si (422), and recording the time-delayed nuclear resonant photons which have less than 20 neV resolution. The result of this measurement is shown in Figure 2. The count rate achieved in this bandpass was  $8 \times 10^7$  photons/sec/5meV. The natural linewidth of  $^{57}\text{Fe}$  nuclei when excited with 14.413 keV photons is 4.8 neV. In other words, there were about 76 photons/sec in one linewidth. The measured detector efficiency of 0.11 reduces this number to 8 photons/sec. Furthermore, we were able to detect only after 20 nsec after the start of nuclear excitation. This corresponds to a calculated loss of about 30 % for this particular sample thickness. The final count rate was about  $5 \pm 2$  photons/sec. The total measurement time was one hour for the Mohr's salt, and two hours for Mohr's salt plus the stainless steel sample.

The Avalanche Photo Diode (APD) detector used in this experiment was made by Advanced Photonics, Inc. The diameter was 16 mm, with a time resolution of 1.1 nsec. The background count rate was less than 0.01 Hz. This and similar detectors have been characterized separately for their efficiency, time response, and dynamic range (7,9).

The forward scattered radiation is coherent in nature. Therefore, samples can be lined up one after another. For example, when a reference

sample is needed for isomer shift measurements the stainless steel foil was simply attached to the Mohr's salt sample.

## RESULTS

The sample is chosen to have a known and a substantial isomer shift with respect to iron in stainless steel. The Mohr's salt is synthesized by oxidizing  $^{57}\text{Fe}$  in a mixture of  $\text{HCl}$  and  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$ . The dried powder was then dissolved in  $(\text{NH}_2\text{OH})_2\cdot\text{H}_2\text{SO}_4$ , and heated to bring the iron into divalent state, and the solution is neutralized by adding  $\text{NH}_4\text{OH}$ . Finally solution is cooled and mixed with anhydrous ethyl alcohol, and centrifuged. The x-ray diffraction pattern proved the formation of  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2\cdot 6\text{H}_2\text{O}$ . However, after a year of storage, the material decomposed into two components. The SMS and transmission Mossbauer spectra of the sample are shown in the composite Figure 3(a) and (b), respectively.

The stainless steel was made from enriched  $^{57}\text{Fe}$  with mixing 55 at% Fe, 25 at % Cr, and 20 % Ni. The mixture was first arc-melted in inert atmosphere and then cold rolled down to 1.44 micron thickness.

The transmission Mossbauer spectra was taken with  $^{57}\text{Co}/\text{Rh}$  source. In all the evaluations we made use of the program package CONUSS (10) that incorporates transmission integral technique to dynamical x-ray scattering. The program is capable of handling diffraction and forward scattering both in the time and the energy domain.

The measurement results in energy and time domain are given in Figure 3. The quantitative evaluation of the spectra are done in Table 1.

**Table 1.** Comparison of results obtained by Synchrotron Mossbauer Spectroscopy, SMS, and transmission Mossbauer spectroscopy experiments

Parameter	SMS	Transmission Mossbauer
<b>Component 1</b>		
isomer shift (mm/sec)	$1.41 \pm 0.02$	$1.36 \pm 0.02$
quadrupole splitting (mm/sec)	$1.71 \pm 0.008$	$1.73 \pm 0.02$
relative weight	$0.79 \pm 0.06$	$0.88 \pm 0.001$
<b>Component 2</b>		
isomer shift ( $\dagger$ ) (mm/sec)	$1.41 \pm 0.24$	$1.41 \pm 0.02$
quadrupole splitting (mm/sec)	$2.83 \pm 0.43$	$2.82 \pm 0.02$
relative weight	$0.21 \pm 0.13$	$0.15 \pm 0.003$
$\chi^2$	3.14	1.46

-----

The isomer shift values in Table 1 are with respect to stainless steel. There is an isomer shift distribution in the stainless steel. It was assumed to be Lorentzian with 0.06 mm/sec (FWHM). The error in the velocity measurements is derived from the error signal of the velocity transducer. The error in time calibration is related to the linearity of time-to-amplitude converter and analog-to-digital converter. It should be noted that the quantum beats due to hyperfine interactions are spread over the entire period of few hundred nanoseconds, and therefore non linearity at a given point tend to average out, making the time domain measurements more accurate than energy domain measurements. The thickness distribution of the Mohr's salt sample was also assumed to be Lorentzian with a width of 5 micron centered around 1.7 micron. This was necessary to obtain a good fit, and indicative of the different nature of the SMS experiments.

## DISCUSSION AND CONCLUSIONS

The comparison of two methodology can be properly done with data sets of similar statistical quality. This is not yet possible with existing synchrotron radiation sources where count rates do not exceed few Hz during regular operations, with few exceptions<sup>(11)</sup>. But one can make a comparison based on the existing data. The Synchrotron Mossbauer Spectrum of stainless steel and Mohr's salt sample together had an integrated count of 114,600 counts with a background of 3200, leading to a signal-to-noise ratio of 35.5, while transmission Mossbauer spectrum had 3,412,000 counts with a background 3,304,000, yielding a signal-to-noise ratio of 0.032. In other words there is a three orders of magnitude difference in statistical quality, in favor of time domain or SMS experiments.

### DATA COLLECTION RATES : Present and Future:

The critical aspect in the overall performance of the SMS set-up is the total energy bandwidth and the flux of the x-rays hitting the detector. These two characteristics combined with the properties of the detector ultimately determines the data collection time. For example, in the experiment performed above,  $8 \times 10^7$  photons/sec/5 meV eventually yielded a count rate of 3-4 Hz delayed photons. The calculated flux for the dedicated undulator (2.7 cm period, 2.5 m long) at APS is  $1.3 \times 10^{13}$  photons/sec/eV/100 mA (see Figure 4). This corresponds to about  $6.5 \times 10^{10}$  photons/sec/5 meV, representing 3 orders of magnitude increase compared to present experiments, and hence reducing the data collection time from few hours to few seconds. However, currently there is no detector to handle the prompt count rates.

This point is graphically illustrated in Figure 5 (a). Here, the expected resonant count rate, and typical data collection time is plotted against effective thickness,  $\beta = n\sigma_0f$ , where  $n$  is the number of  $^{57}\text{Fe}$  atoms/cm<sup>2</sup>,

$\sigma_0=2.36 \times 10^{-15} \text{ cm}^2$ , and  $f$  is the recoil free fraction, for both enriched and natural iron samples. Due to present detector difficulties, it will not be possible to reduce the data collection times below 150 seconds for this particular Mohr's salt sample.

It is possible to solve this problem for some cases by taking advantage of the polarized nature of the synchrotron radiation, and the vertically and horizontally collimated nature of the undulator based sources. By employing a polarizer/analyzer monochromator, based on Si (840) crystals with a Bragg angle of  $45.1^\circ$  at 14413 eV, one can solve this problem rather elegantly. This method, explicitly discussed before <sup>(12)</sup>, and proven in principle <sup>(13)</sup>, relies on the high optical activity of the Mossbauer medium, and high polarization selectivity of Bragg diffraction near  $45^\circ$  angles <sup>(14)</sup>. Figure 5 (b) gives the calculation for the case where a polarizer/analyzer is used. Then, with a polarization rejection ratio of  $10^8$  it will be possible to reduce the data collection times to few seconds level.

#### ACKNOWLEDGMENTS

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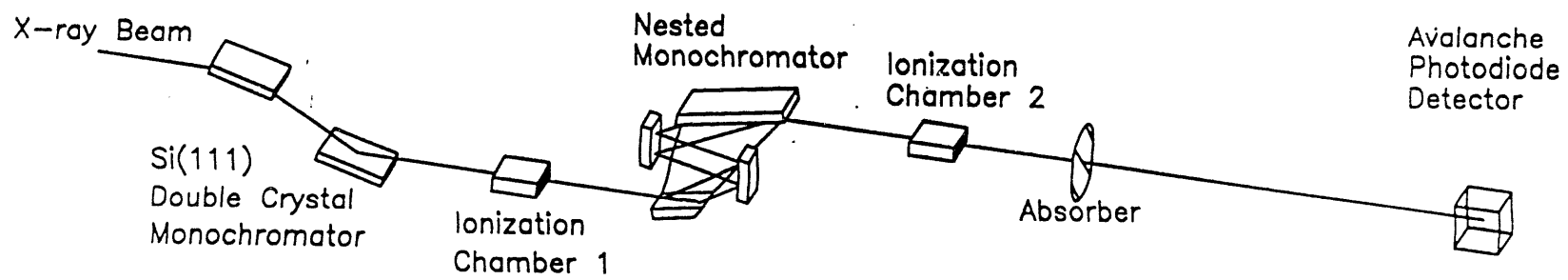


Figure 1. Schematic layout of the forward scattering experiment.

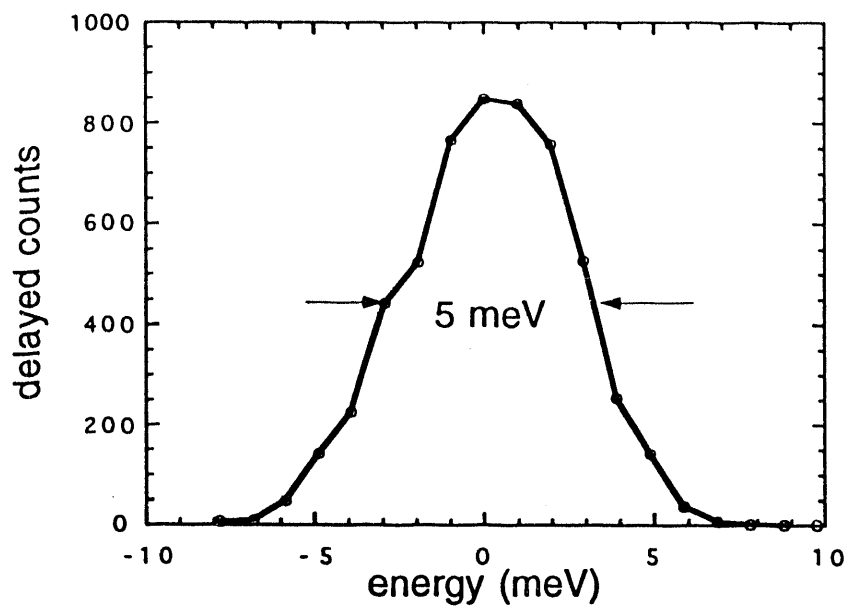


Figure 2. The 5 meV (FWHM) energy resolution of the Si (4 2 2)- Si (10 6 4) nested monochromator, measured by nuclear delayed photons.

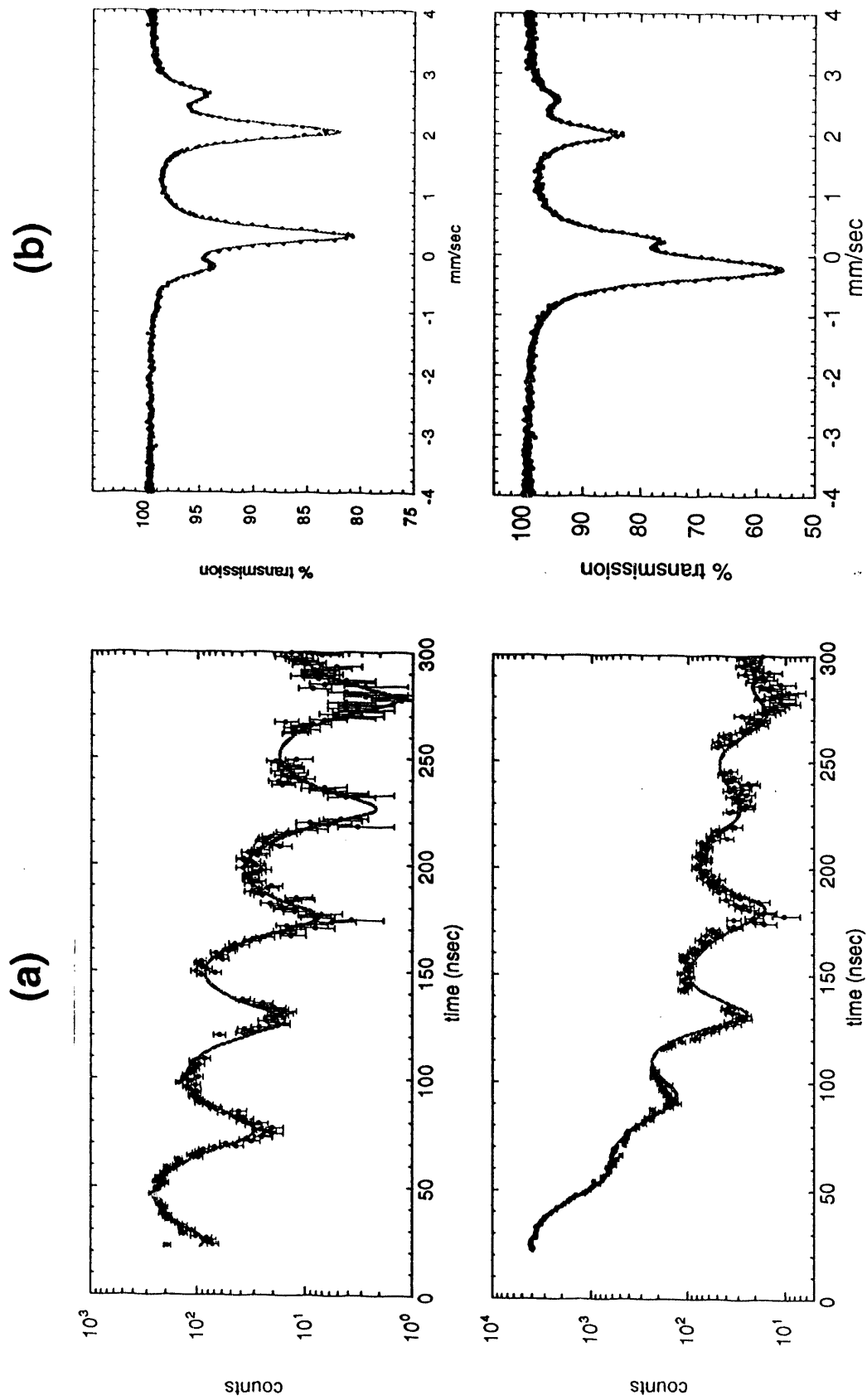


Figure 3. (a) The Synchrotron Mossbauer Spectroscopy, SMS, and (b) transmission Mossbauer Spectroscopy results of Mohr's salt (upper figures) and Mohr's salt plus stainless steel (bottom figures). The missing data points around 110, 140, and 250 ns are where the parasitic bunches in the synchrotron contribute significantly, and therefore they are blocked out..

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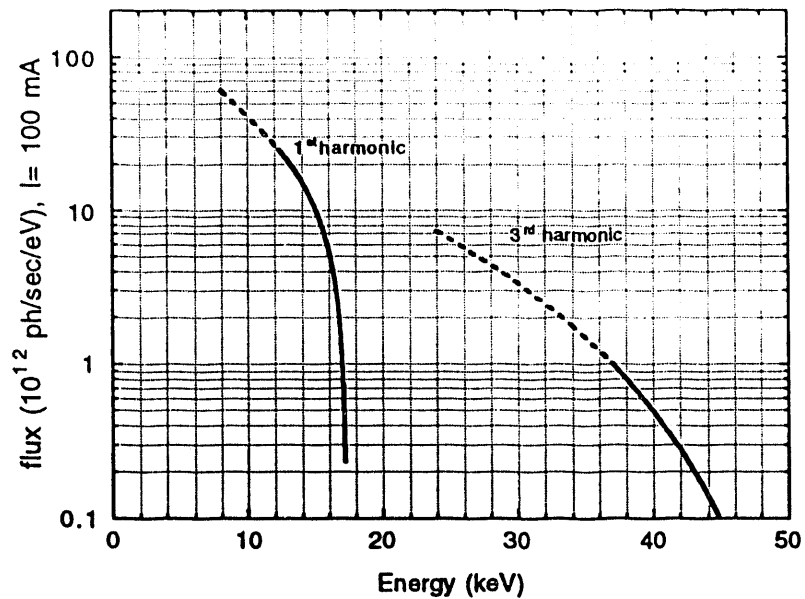


Figure 4. The calculated flux in the central cone from 2.7 cm period undulator at APS. The solid lines show the tunability range with 14.5 mm minimum gap, and dashed lines are for 10.5 mm gap.

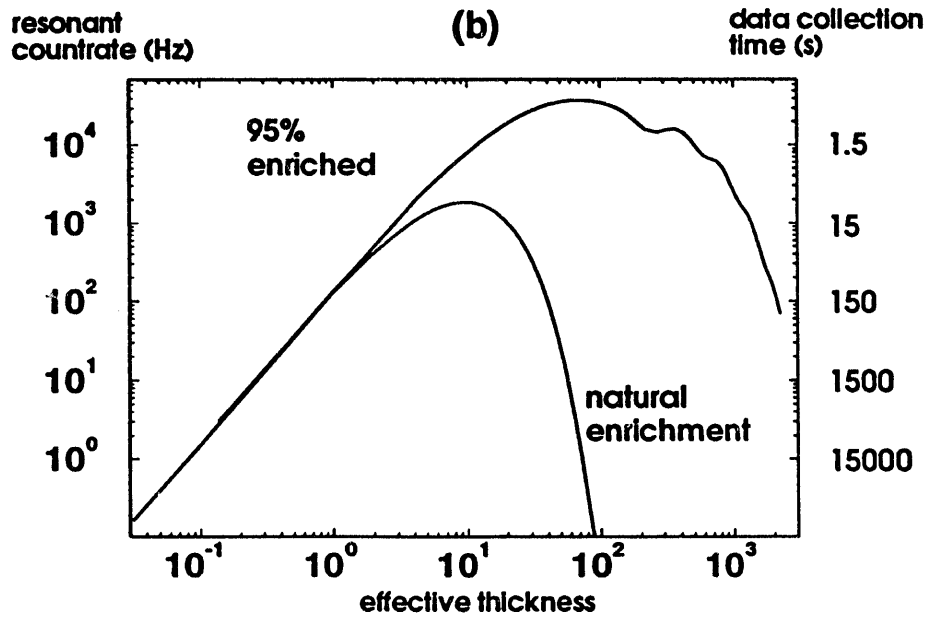
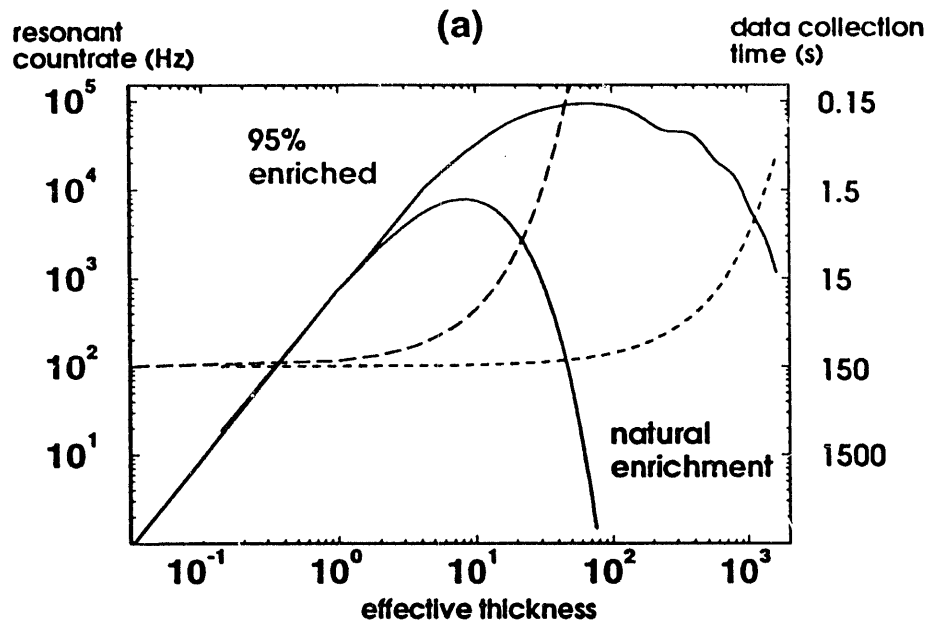


Figure 5. Calculated count rates (right y-axis), and data collection times (left y-axis) to obtain spectra of similar statistical quality as in Figure 3. (a) With a 5 meV bandpass nested type monochromator, and (b) with polarizer/analyzer type monochromator. The dashed lines in (a) indicate the limit at which current detectors will saturate with a 5 meV bandpass.

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