

# Study of tin amalgam mirrors by $^{119}\text{Sn}$ Mössbauer spectroscopy and other analytical methods

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**Abstract** From the beginning of the 16<sup>th</sup> until the end of the 19<sup>th</sup> century the most widely used mirrors consisted of a pane of glass backed with a reflecting layer of tin-mercury amalgam. They were made by sliding the glass pane over a tin foil covered with liquid mercury. After removal of the superfluous mercury, tin amalgam formed slowly at ambient temperature and yielded a reflecting layer adhering to the surface of the glass. Such mirrors often deteriorate in the course of time by oxidation of the tin in the amalgam to stannous or stannic oxide.  $^{119}\text{Sn}$  Mössbauer spectroscopy, scanning electron microscopy, micro-XRF and X-ray diffraction have been used to study this deterioration process. The studied specimens were a modern mirror made for the reconstruction of the Green Vault in Dresden in the early 2000s, two rather well preserved German mirrors from the 17<sup>th</sup> and 19<sup>th</sup> centuries and several strongly deteriorated specimens of Baroque mirrors from the south of Spain. The modern mirror consists mainly of a  $\text{Sn}_{0.9}\text{Hg}_{0.1}$  amalgam with only 2 % of  $\text{SnO}_2$ . The older German mirrors showed more pronounced oxidation, containing 12 and 15 % of  $\text{SnO}_2$ , which did not noticeably impair their reflectivity. In the samples from the Spanish mirrors at best a few percent of metallic phase was left. The majority of the tin had oxidised to  $\text{SnO}_2$ , but between 8 and 20 % of the tin was present as  $\text{SnO}$ . X-ray diffraction yielded similar results and micro-XRF mapping using synchrotron radiation for excitation gave information on the distribution of Sn and Hg in the reflecting layer of the mirrors.

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## 1 Introduction

Flat glass panes backed with a reflecting layer of tin amalgam were the most widespread mirrors from the 16<sup>th</sup> century until the end of the 19<sup>th</sup> century. Then they were substituted by silver mirrors produced by the wet chemical method developed by J. v. Liebig in the middle of the 19<sup>th</sup> century. The main production site of tin amalgam mirrors was Venice until, under the reign of Louis XIV, a manufacture of mirrors was founded in Paris. The French company developed a novel method for casting mirror glass, which was one of the reasons why in the end of the 17<sup>th</sup> century the centre of mirror production shifted to France. Later the production of amalgam mirrors spread to many other countries.

Tin amalgam mirrors were made by sliding a flat and polished glass pane over a tin foil laid out on a flat marble table and covered with a few millimetres of liquid mercury. The superfluous mercury was pressed out and within days the tin converted to a tin amalgam that adhered well to the glass, hardened in the course of time and formed a rather enduring reflecting layer [1].

Today, tin amalgam mirrors are mainly found in churches, palaces and museums. They are no longer produced, largely because of labour protection regulations that make the use of mercury difficult and require expensive protection measures. Occasionally, however, tin amalgam mirrors are still made today for the restoration of old interiors, when the original amalgam mirrors were destroyed or have deteriorated in the course of time. Modern silver mirrors may be deemed inadequate to capture the former flair of interiors because they reflect more light than the original amalgam mirrors [2]. For the reconstruction of the Green Vault in Dresden, the treasure chamber of August the Strong, elector of Saxony and king of Poland (1670-1733), a German company<sup>1</sup> developed a method for producing tin amalgam mirrors observing modern labour protection rules. The Green Vault had been richly furnished with tin amalgam mirrors, most of which were destroyed during World War II. It was restored after the German re-unification and reopened in 2006, rebuilt with newly produced tin mirrors, some of which were made by the tin amalgam process, while others were produced by sputtering methods [2, 3].

Tin amalgam mirrors are known to consist of grains of tin amalgam with the interstitial spaces filled with liquid mercury containing only very little tin [1]. In the course of time, the mercury evaporates or, due to gravity, slowly sinks to the lower rim of the mirror, where it may even form droplets of mercury in the frame. Depending on atmospheric conditions, the amalgam may also lose mercury by evaporation, and the resulting small tin particles may oxidise [3], which causes the mirrors to become cloudy. These processes have been studied by microscopic methods and X-ray diffraction [4–6]. In the following, we refer to some of these results and report on a <sup>119</sup>Sn Mössbauer study of samples from tin amalgam mirrors in different states of deterioration.

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**Table 1** Mössbauer parameters for tin amalgam mirrors and reference materials

Sample	Absorber Thickness (mg/cm <sup>2</sup> )	QS (mm/s)	IS (mm/s)	Relative area (%)	Assignment
Modern, Green Vault Dresden	7.9	0.64(1)	2.63(1)	98.6(2)	Sn <sub>0.9</sub> Hg <sub>0.1</sub>
German, 2 <sup>nd</sup> half 19 <sup>th</sup> century	7.6	0.69(1)	2.63(2)	87.8(2)	Sn <sub>0.9</sub> Hg <sub>0.1</sub>
		0.57(2)	-0.01(1)	12.2(2)	SnO <sub>2</sub>
German, 17 <sup>th</sup> century	8.7	0.64(1)	2.62(2)	85.0(2)	Sn <sub>0.9</sub> Hg <sub>0.1</sub>
		0.56(2)	0.00(6)	15.0(2)	SnO <sub>2</sub>
Iglesia Santa Ana, Sevilla, 18 <sup>th</sup> century	8.6	0.60(1)	-0.01(1)	80.2(2)	SnO <sub>2</sub>
		1.40(1)	2.66(2)	19.8(2)	SnO
Christo del Llano Hermitage, Jaén, 17 <sup>th</sup> century	5.2	0.60(1)	-0.01(1)	85.2(2)	SnO <sub>2</sub>
		1.42(1)	2.67(1)	14.8(2)	SnO
Camerin Virgen del Rosario, Granada, 18 <sup>th</sup> century, No. 2	8.3	0.59(1)	-0.01(1)	91.9(2)	SnO <sub>2</sub>
		1.45(1)	2.65(1)	8.1(2)	SnO
Camerin Virgen del Rosario, Granada 18 <sup>th</sup> century, No. 6	27.2*	0.58(1)	-0.01(1)	83.0(8)	SnO <sub>2</sub>
		1.38(4)	2.65(2)	13.7(8)	SnO
		0	2.54	3.3(6)	Sn metal
SnO	10.2	1.37(1)	2.67(1)	97.4(2)	SnO
		0.49(1)	-0.2(1)	2.6(2)	SnO <sub>2</sub>
SnO <sub>2</sub>	2.4	0.50(1)	-0.03(1)	100	SnO <sub>2</sub>
Metallic tin	7.9	0.	2.54(1)	100	Sn metal

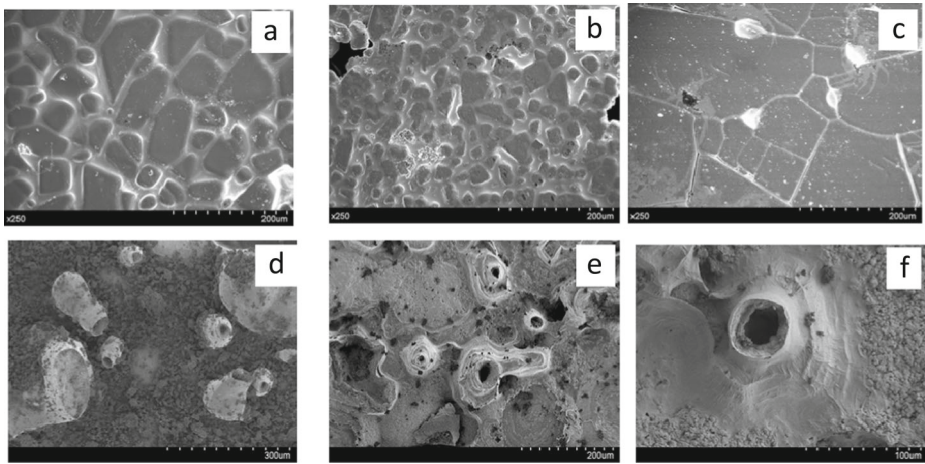
Last digit errors are given in parentheses. Where no errors are given, the parameter was fixed in the least squares fitting procedure. IS is the isomer shift with respect to the CaSnO<sub>3</sub> source at 4.2 K. QS is the electric quadrupole splitting

\*Including glass from the mirror

## 2 Samples and experiments

A total of seven samples from amalgam mirrors were studied by Mössbauer spectroscopy (Table 1). One of them is a specimen of the mirrors produced for the reconstruction of the Green Vault in Dresden. Two more rather well kept specimens are also of German origin, stemming from the 17<sup>th</sup> and the 19<sup>th</sup> century. Four specimens are from strongly corroded Baroque mirrors from the south of Spain from the 17<sup>th</sup> and 18<sup>th</sup> century, which were studied by various analytical methods previously [4–7]. A description of these mirrors is given in Ref. [7]. The specimens available for Mössbauer spectroscopy in this case were small glass fragments bearing the remnants of strongly corroded amalgam layers.

The material for Mössbauer spectroscopy was removed from small fragments of glass of less than a square centimeter in size, which had been recovered during the restoration of the mirrors. In the case of a sample from the Camerin Virgen del Rosario in Granada the whole glass fragment with remnants of the reflecting layer was powdered to make the Mössbauer



**Fig. 1** SEM image of the surface morphology of (a) the modern mirror for the reconstructed Green Vault, Dresden (b) the German mirror from the 2<sup>nd</sup> half of the 19<sup>th</sup> century (c) the German mirror of the 17<sup>th</sup> century, (d) the 18<sup>th</sup> century Spanish mirror from Sevilla, (e) the 17<sup>th</sup> century Spanish mirror from Jaén, and (f) the 18<sup>th</sup> century Spanish mirror from Granada

absorber. The absorber holders were Lucite capsules with a diameter of 10 mm, which means that one needs no more than 5 mg of the reflecting layer to obtain good Mössbauer spectra. To make homogeneous absorbers, the mirror material was mixed with quartz glass powder and ground in a mortar together with it.

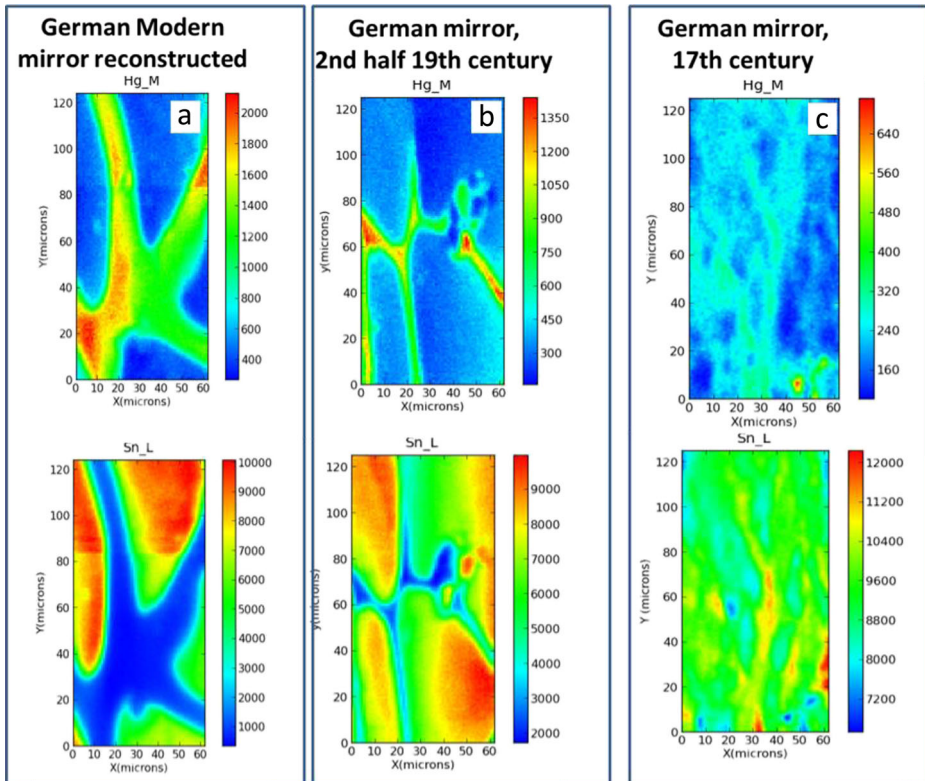
The Mössbauer spectra were taken at 4.2 K in a liquid He bath cryostat in which the source of about 10 mCi  $^{119\text{m}}\text{Sn}$  in  $\text{CaSnO}_3$  was also cooled to liquid He temperature. The velocity drive operated with a sinusoidal waveform. The gamma rays were detected with a 2 mm thick  $\text{NaI(Tl)}$  scintillation detector. A 35  $\mu\text{m}$  thick Pd absorber was used to attenuate the K X-rays of tin. The spectra were fitted with appropriate superpositions of Lorentzian lines.

Scanning electron microscopy (SEM) analyses of the morphology of the amalgam mirrors were carried out in a SEM-FEG Hitachi S4800 operating at a voltage of 20 keV.

Micro synchrotron X-ray fluorescence ( $\mu\text{XRF}$ ) measurements of the distribution of tin and mercury in the mirrors were performed in Grenoble at the microprobe station ID21 [8] of the ESRF. The beam was focused with zone plates to a spot size of 0.8  $\mu\text{m}$  x 1.5  $\mu\text{m}$  at a flux of  $1.45 \times 10^8$  photons/s. The focused beam remained fixed while the sample was raster scanned horizontally and vertically to obtain two-dimensional images. An energy of 7.2 keV was chosen for excitation and the L lines of tin and the M lines of mercury were used for element analysis. The measurements were performed under vacuum to avoid scattering and absorption in air. The X-rays were detected with a 30 mm<sup>2</sup> Ge solid state detector with an energy resolution of 135 eV at 6 keV.

### 3 Results and discussion

The reflecting layer of new amalgam mirrors consists of islands of the tin amalgam and films of liquid mercury between them [1, 2]. According to the Sn-Hg phase diagram [9], the liquid mercury contains practically no tin and hence will be invisible to Mössbauer spectroscopy

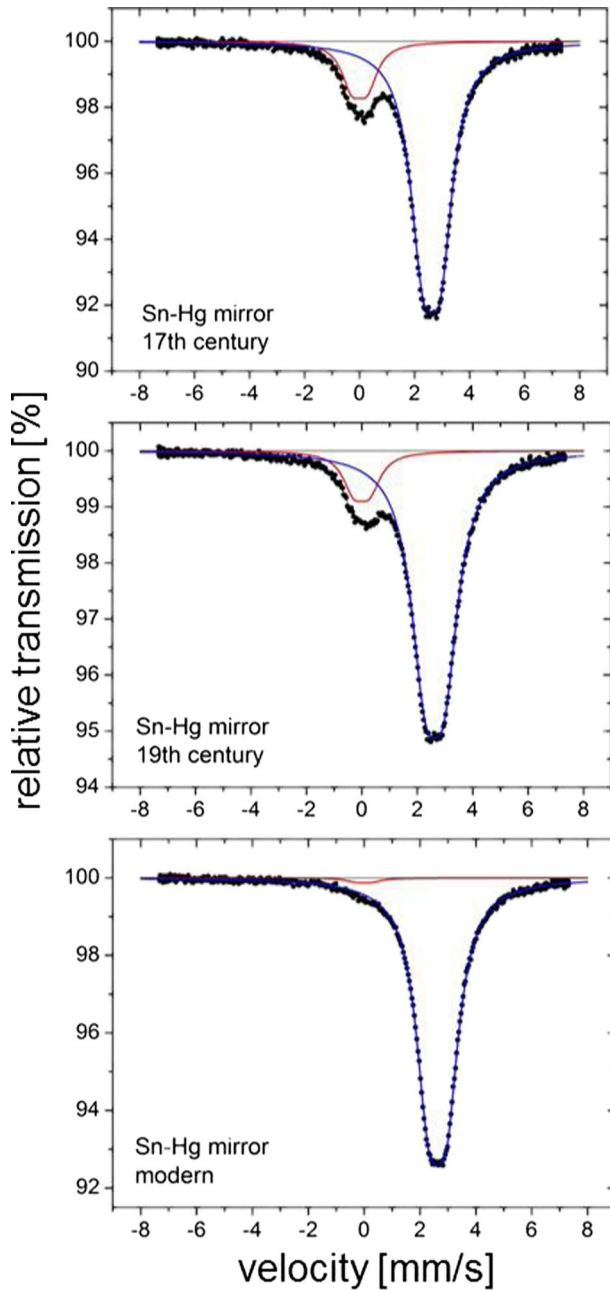


**Fig. 2** Micro-XRF mappings of the distribution of the Hg and Sn obtained for an excitation energy of 7.3 keV for  $60 \times 120 \mu\text{m}$  regions for the recent mirror for the reconstruction of the Green Vault in Dresden (a), and for the well-preserved German mirrors from the 19<sup>th</sup> and 17<sup>th</sup> century (b,c). One sees the loss of mercury and the disappearance of the structure of amalgam islands and films of practically pure mercury between them, due to ageing

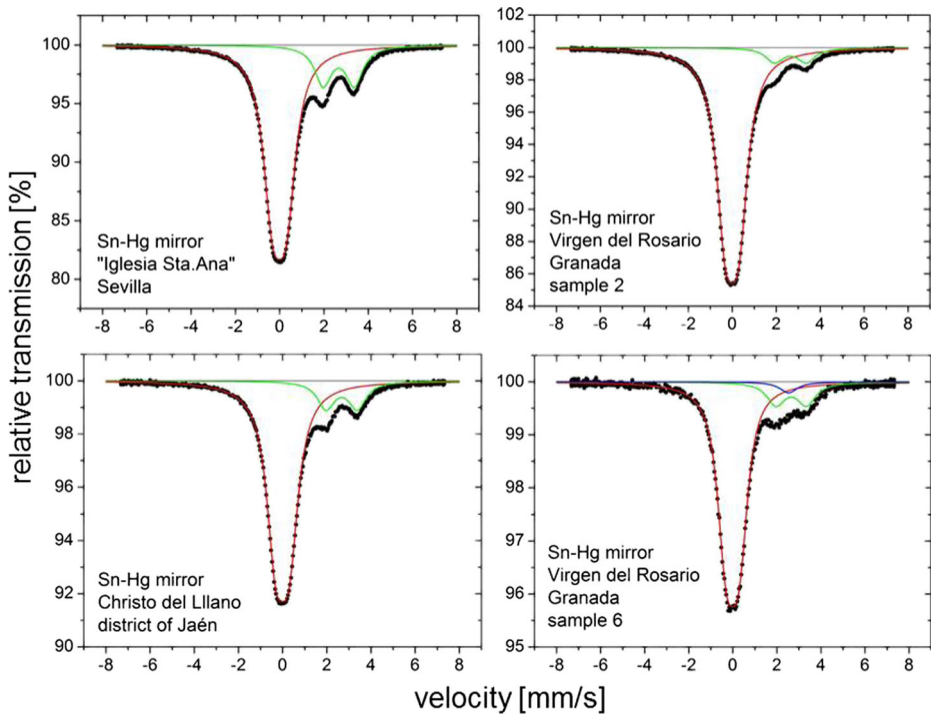
even in the frozen state at low temperatures. In the course of time, the liquid mercury will disappear due to gravity, which causes it to sink to the lower rim of the mirror, or due to evaporation. This leaves small tin particles that oxidize easily. The simultaneous presence of metallic tin and the tin amalgam with the approximate composition  $\text{Sn}_{0.9}\text{Hg}_{0.1}$  has been demonstrated by X-ray diffraction [5]. X-ray diffraction has also been used to analyze the oxidation to  $\text{SnO}$  and  $\text{SnO}_2$  [4–7].

### 3.1 Scanning electron microscopy

The scanning electron micrographs shown in Fig. 1 show the surface morphology of amalgam mirrors in various states of deterioration. In the freshly prepared specimen the islands of tin amalgam and the mercury-rich phase between them are clearly visible (Fig. 1a). The change of this structure with time can be seen in the mirrors from the 19<sup>th</sup> and 17<sup>th</sup> centuries (Fig. 1b and c), which illustrate the gradual disappearance of the mercury-rich boundaries. The Spanish mirrors (Fig. 1, d-f) are in a much more advanced stage of deterioration. The mercury has largely disappeared due to evaporation, leaving finely divided particles of tin, whose presence has been demonstrated by X-ray diffraction [5, 6].



**Fig. 3**  $^{119}\text{Sn}$  Mössbauer spectra taken at 4.2 K for samples of well preserved German tin amalgam mirrors from the 17<sup>th</sup> and 19<sup>th</sup> century (top and middle) and from the reconstruction of the Green Vault in Dresden (bottom)



**Fig. 4**  $^{119}\text{Sn}$  Mössbauer spectra taken at 4.2 K for samples of severely corroded Spanish tin amalgam mirrors

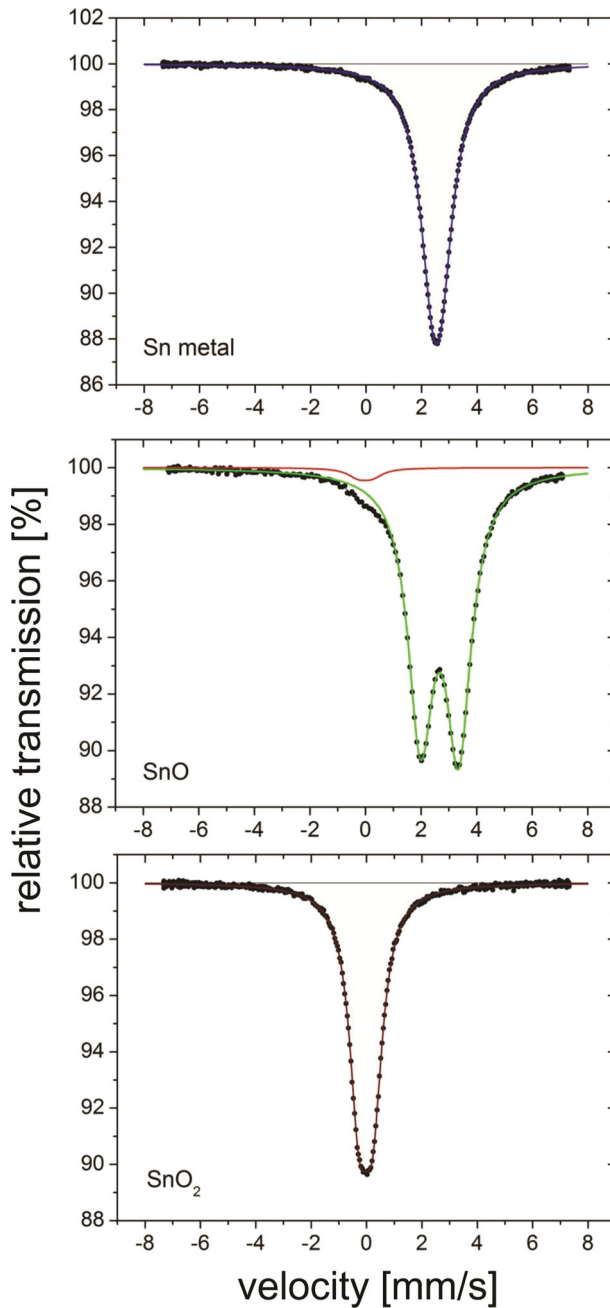
### 3.2 Micro-XRF Synchrotron radiation based technique

To further study the distribution of tin and mercury in the reflecting layer, elemental mappings were obtained for the three German amalgam mirrors from the reconstruction of the Green Vault and from the 19<sup>th</sup> and 17<sup>th</sup> centuries (Fig. 2). In the newly made mirror, the structure of amalgam islands containing relatively little mercury and the films of mercury in between is well visible. In the mirror from the 19<sup>th</sup> century, this structure is already impaired, and in the mirror from the 17<sup>th</sup> century it has virtually disappeared and the overall content of mercury is largely diminished.

### 3.3 Mössbauer spectroscopy

Figure 3 shows the Mössbauer spectra of the three German mirrors, Fig. 4 the spectra of four samples of Spanish mirrors and Fig. 5 shows reference spectra of SnO, SnO<sub>2</sub> and metallic tin. The Mössbauer parameters obtained by the least squares fits are summarized in Table 1.

The German mirrors all show a dominant component that can be attributed to tin amalgam with the approximate composition Sn<sub>0.9</sub>Hg<sub>0.1</sub> on the basis of its Mössbauer parameters. In the past, tin amalgams have been studied by Mössbauer spectroscopy in the context of dental amalgams [10, 11]. Dubois et al. [10] report a marginal dependence of the Mössbauer parameters of Sn-Hg amalgam on the exact composition with an isomer shift of about 2.65 mm/s with respect to BaSnO<sub>3</sub> and a small quadrupole splitting of about 0.55 mm/s. These parameters agree very well with the ones obtained for the mirrors, except for a slightly



**Fig. 5**  $^{119}\text{Sn}$  Mössbauer spectra taken at 4.2 K for reference materials: Metallic tin, SnO, and SnO<sub>2</sub>. The SnO contains a small impurity of SnO<sub>2</sub>

larger quadrupole splitting in the latter. The isomer shift of the amalgam is only marginally larger than that of metallic tin (Table 1), rendering a distinction of the two on the basis



of the isomer shifts practically impossible. Metallic tin, however, does not show a noticeable quadrupole splitting, which may serve as a distinction. We thus may conclude that the German mirrors all consist mainly of the tin amalgam phase. There is, however, a small contribution of  $\text{SnO}_2$  present in all of them. This is nearly negligible in the modern mirror, but amounts to 12 % and 15 % of the spectral area in the older German mirrors. Contrary to the Spanish mirrors described below,  $\text{SnO}$  is not observed in the German mirrors, but a small contribution of it would be difficult to observe below the dominant component of tin amalgam. One therefore cannot tell whether  $\text{SnO}$  is present as a minor intermediate oxidation product in the German mirrors.

The severely corroded Spanish mirrors show very different Mössbauer spectra. In these specimens there is practically no metallic phase present any more. The main component is always  $\text{SnO}_2$ , but now there is a minor component of  $\text{SnO}$ , which appears as an intermediate product of the corrosion process. It has a positive isomer shift that is practically identical to that of the tin amalgam. However, since it has a rather large quadrupole splitting (Table 1), it can easily be distinguished from the amalgam phase and from metallic tin. The intensity of the  $\text{SnO}$  component in the four Spanish mirrors (Fig. 4) is between 8 % and 20 % of the spectral area. The  $\text{SnO}$  quadrupole doublet was assumed to be symmetrical, although in the reference spectrum (Fig. 5) a small asymmetry is visible. Herber [12] observed an even stronger asymmetry in  $\text{SnO}$  and concluded from measurements of the temperature dependence that it is due to texture rather than to an anisotropy of the Lamb-Mössbauer factor. In the mirrors the presence of the strong component of  $\text{SnO}_2$  renders the detection of small asymmetries of the  $\text{SnO}$  doublet virtually impossible.

Sample 6 from the Camerin Virgen del Rosario in Granada is the only case where a very weak metallic contribution is still just barely visible in the Mössbauer spectrum. The spectrum was fitted with fixed isomer shifts and quadrupole splittings for the metallic phase. Fits with a single line with an isomer shift corresponding to that of metallic tin (Table 1) yielded a slightly better agreement with the data than the assumption of an amalgam phase. It may thus be a case where the tin became metallic before oxidation, though one cannot be certain of this because of the low intensity of the resonance from the metallic phase.

To convert the relative intensities in the Mössbauer patterns into the relative masses of tin in the individual components, one has to take the Lamb-Mössbauer factors  $f$  of the individual phases into account, since the areas in the Mössbauer spectra are proportional to these and the masses of tin. For the  $f$ -factor of the  $\text{Sn}_{\sim 0.9}\text{Hg}_{\sim 0.1}$  amalgam at 77 K Dubois et al. [10] give  $f = 0.53$ . This corresponds to a Debye temperature of about 175 K and allows one to extrapolate to  $f \approx 0.74$  at 4.2 K using the Debye model. The  $f$ -factor for metallic tin at 4.2 K has been determined as  $f = 0.72 \pm 0.01$  by Hohenemser [13]. For  $\text{SnO}$  Herber [12] found  $f = 0.74 \pm 0.03$  at 78 K. Using the Debye model, this extrapolates to  $f \approx 0.82$  at 4.2 K. For  $\text{SnO}_2$  Allen et al. [10] give a value of  $f = 0.77$  at 77 K which extrapolates to about  $f \approx 0.83$  at 4.2 K. Even if these values for the  $f$ -factors are subject to some error, the conclusion is that they are quite similar at 4.2 K and that only a minor uncertainty results if one neglects the correction for the individual  $f$ -factors altogether.

## 4 Conclusions

$^{119}\text{Sn}$  Mössbauer spectroscopy is well suited for studying the state of the tin amalgam in tin amalgam mirrors. It is easy to obtain the relative amounts of the individual phases from the intensities in the Mössbauer patterns.

Only about 5 mg of tin amalgam or its deterioration products are needed to obtain good Mössbauer spectra. Glass fragments containing material from the reflecting layer can be crushed and the powder used as Mössbauer absorber. The spectra afford a reliable distinction between the  $\text{Sn}_{0.9}\text{Hg}_{0.1}$  amalgam and the main deterioration products,  $\text{SnO}_2$  and  $\text{SnO}$ . Metallic tin and the tin amalgam are more difficult to distinguish, particularly when they are a minority phase in the presence of a stronger SnO component.

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