

CEMS study of tin in the hot end coatings of glass containers

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Tin oxide coatings are applied to glass containers as adhesion promoters for the organic lubricants. Here, room temperature conversion electron Mössbauer spectroscopy (CEMS) is used to analyse a range of tin oxide coated containers. Readable CEMS curves could be obtained even for the thinnest (30 CTU or about 6 nm) coatings. The hyperfine parameters calculated from the spectral curves show that tin is tetravalent in crystalline form with a preferential grain orientation, which is reduced on annealing. The presence of tin in other oxidation states and dissolved in the matrix was excluded.

CEMS-Untersuchung von Zinn in heißendvergüteten Glasflaschen

Glasflaschen werden mit Zinnoxid vergütet, wobei die Oxidvergütung als Haftvermittler für organische Schmiermittel dient. In der vorliegenden Arbeit wird die Conversion Electron Mössbauer Spectroscopy (Mössbauer-Spektroskopie der Umwandlungselektronen) bei Raumtemperatur verwendet, um eine Reihe heißendvergüteter Flaschen zu untersuchen. Lesbare CEMS-Kurven werden auch für die dünnsten (30 CTU, d.h. ungefähr 6 nm) Schichten erhalten. Die aus den spektralen Kurven berechneten Hyperfeinparameter zeigen, daß Zinn vierwertig und in kristalliner Form vorliegt. Die einzelnen Kristalle sind vorzugsweise zur Oberfläche orientiert, wobei die Orientierung nach einer Wärmebehandlung abnimmt. Die Anwesenheit von Zinn in anderen Oxidationszuständen bzw. gelöst in der Glasmatrix wurde ausgeschlossen.

1. Introduction

Hot end coatings are thin metal oxide layers obtained by decomposition of metal salts in contact with the hot container surface shortly after forming. In combination with cold end coatings (organic lubricants applied as the container exits from the annealing lehr [1]), they protect the glass surface from the damage produced by sliding contacts on production lines and during transport [2 to 4]. The present study concentrates on the material most frequently used in Italy, i.e. tin oxide produced by thermal decomposition of SnCl_4 or of ButylSnCl_3 vapours.

An accurate knowledge of the composition and structure of tin oxide coatings is necessary for a rational approach to several aspects of their behaviour, ranging from bottle strength and lubrication to metal cap corrosion, release torque and so on [2, 4 and 5]. Moreover, a correct interpretation of the signals read by various surface analytical techniques (such as XPS, SIMS and electron probe microanalysis) requires a preliminary knowledge of the film composition (stoichiometry, impurities) and structure (discrete or subject to interdiffusion with the substrate, compact or porous and columnar) [6 and 7].

In the past, various theories were published attributing the experimentally determined properties of tin oxide coatings to postulated structural and chemical features. For example the improved bottle strength was attributed to healing of Griffith's flaws, surface compression or inhibited stress corrosion [2] and the stable bond of the tin oxide coating with the glass was attributed to interdiffusion [8 to 10]. According to some patents the electrochemical reactions between the metal and the oxide leading to metal cap corrosion might be favoured by a conductive or semiconductive character of the coatings, possibly associated with the contemporary presence of tin, SnO and SnO_2 [11 to 13]. However, no reliable experimental evidence was published in support of such hypotheses: generally the low coverage and the curved substrate frustrated most attempts to actually analyse the industrial production.

The only well established property of industrial hot end coatings is their discontinuous structure, due to the presence of NaCl crystals (with dimensions up to some μm) formed by a reaction of HCl originating from the decomposition of the gaseous precursor (SnCl_4 or organo-chloro-tin) with the glass surface. Such crystals grow during the coating process, interrupting the continuity of the tin oxide coating and sublimate during an-

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nealing, leaving square holes of bare glass [2 and 14]. For the rest, most of the published evidence is based on experiments performed on rather thick films (several 100 nm) deposited by some laboratory CVD technique on microscope slides [2, 8, 9, 15 to 17]. Such results can be applied to industrial coatings only with great caution, since the different substrate, coating and annealing conditions may affect the character of the resulting films. In order to overcome such problems, Stazione Sperimentale del Vetro dedicated a research program to industrially coated containers [1, 6, 7, 14 and 18]. In [6] XPS was used to analyze film impurities: sodium (carbonates and chlorides), carbon (hydrocarbons and carbonates) and chlorine (NaCl) were detected. An attempt to establish the oxidation state of tin with careful XPS measurements failed because the lines corresponding to stannous and stannic tin are nearly coincident [6]. This conclusion is in agreement with the recent literature [19] and disproves earlier reports [9]. Attempts to obtain further evidence on this point by measuring the Sn/O ratio using XPS or electron probe microanalysis (EPMA) yielded hardly interpretable results, due to contamination of the film with alkali carbonates [6]. Careful studies with X-ray diffraction (XRD) analysis [6] suggested that coatings ≥ 50 CTU¹⁾ have the structure of crystalline cassiterite (SnO₂). Below this coverage, the sensitivity was insufficient to detect the weaker diffraction peaks and to distinguish between the different crystalline forms of tin oxide. Finally, tin depth profiles obtained with XPS analysis during sequential sputtering [6] showed that the degree of interdiffusion with the substrate is quite limited (at best, of the same order as the film thickness).

In [18] industrially produced tin oxide container coatings were characterized using XPS and SIMS. The presence of contaminants containing sodium, carbon and chlorine was confirmed. Moreover, it was shown that analytical procedures using ion sputtering to obtain depth profiles tend to broaden the film-substrate interface region and to alter the Sn/O ratio. Such results add weight to the conclusion of Passamonti et al. [6] about the limited interdiffusion with the substrate, but leave open the question about the tin oxide stoichiometry.

In [7] it was shown that the CTU¹⁾ readings obtained with the hot end coating meter (HECM) manufactured by AGR, Inc., Butler, PA (USA) during industrial production controls are proportional to the tin oxide coverage determined with electron probe microanalysis. In particular, it was shown that 1 CTU corresponds to 0.13 $\mu\text{g SnO}_2/\text{cm}^2$. A typical coverage of 30 to 50 CTU corresponds to 4 to 6.7 $\mu\text{g SnO}_2/\text{cm}^2$. If the film had the same density as crystalline cassiterite, i.e. 7 g/cm³, the corresponding film thickness would be 5.7 to 9.5 nm.

¹⁾ Note. In container production, the thickness of tin oxide coatings is normally expressed in terms of CTU, or Coating Thickness Units measured with the Hot End Coating Meter manufactured by AGR. Equivalent thickness and coverage values are given in [7].

Table 1. Characteristics of the container samples analysed

sample no.	bottle type and capacity	HECM reading in CTU	heat treatments
1	mineral water, 1 l	30	as received
2	fruit juice, 0.125 l	50	as received
3	mineral water, 1 l	100	as received
4	mineral water, 1 l	100	as received
5	mineral water, 1 l	100	10 min at 700 °C

Even admitting that the actual density is probably smaller, this result shows that hot end coatings for containers are much thinner than the tin oxide coatings used for optical and electronic applications.

In an attempt to simulate the behaviour of industrial hot end coatings, Sanyal and Mukerji [16] and Mukerji and Sanyal [17] used Mössbauer spectroscopy in transmission to analyse powdered microscope slides treated by CVD with SnCl₄. The obtained Mössbauer spectra were typical of tetravalent tin, regardless of coating temperatures. The sharpening of the spectrum observed when the coating process took place at higher temperatures was attributed to variations of coordination (from tetragonal to octahedral) accompanying the diffusion of tin into the matrix. In order to apply Mössbauer spectroscopy to industrial tin oxide coatings, it was decided to use in the present study conversion electron Mössbauer spectroscopy (CEMS) suitable to evaluate the electronic structure of tin in surface coatings and layers. In previous studies this technique was found suitable to detect and distinguish both Sn(II) and Sn(IV) in the surface layers of float glass [20 to 22].

2. Experimental

2.1 Samples

Five container samples from various plants industrially coated using SnCl₄ and annealed were selected. Their characteristics are reported in table 1. The bottles, with capacities between 0.1 and 1.0 l, came from various plants. Sample 5 is a container section cut from a bottle coated with 100 CTU, heated up to 700 °C in an electrical furnace, treated for 10 min, then slowly cooled. For comparison, also a neighbouring section which had not received the heat treatment was examined (sample 4).

2.2 Determination of the tin oxide coating coverage

The tin oxide coverage was assessed using the hot end coating meter [7]. The coverage is expressed in terms of CTU (coating thickness units). 1 CTU is equivalent to 0.13 $\mu\text{g SnO}_2/\text{cm}^2$ [7]. Container sections with CTU readings ranging from 30 to 100 CTU were selected for analysis (see table 1).

2.3 Mössbauer spectroscopy

Samples with a size of (20×20) m² previously analysed with the HECM were cut from the bottle and carefully cleaned with isopropanol to remove grease and residues of cold end coatings. Conversion electron Mössbauer spectroscopy (CEMS) measurements were carried out by means of a standard Mössbauer spectrometer with a gamma ray source of ^{119m}Sn in BaSnO₃ matrix and a gas flowing (95 % helium, 5 % CH₄) proportional counter to detect conversion electrons. The information achieved in this way regards tin atoms near the surface. The escape depth of conversion electrons emitted after resonant absorption of primary gamma rays is about 200 nm. In the present case the low tin coverage requires a measuring time of 2 or 3 d using a source of about 3 millicurie activity. In such conditions it is possible to achieve acceptable statistics, allowing to identify the peaks of both Sn(II) and Sn(IV) species and to calculate their hyperfine parameters. The velocity calibration was made by collecting simultaneously a spectrum of metallic iron with a ⁵⁷Co:Rh source mounted on the other side of the velocity transducer. A standard least squares minimization routine was used to fit the spectral profiles as a superposition of Lorentzian lines. The measurements were performed on slightly curved glass substrates cut from container walls. The only consequence is that the obtained spectra are prevailingly due to the part of the sample nearest to the sensitive element of the counter (the wire(s) if a proportional counter is used, as in the present case).

The physical meaning of the hyperfine parameters can be summarized as follows [23]. The isomer shift δ is related to the *s* electron density at the tin nucleus and reflects the valence state, the ionicity of the tin bonds and the interatomic distances. The quadrupole splitting Δ arises from the presence of an electric field gradient at the tin nucleus and is then related to asymmetric charge distribution of the valence *p* electrons around the tin site. The linewidth Γ is normally an indication, when higher than the natural (or minimum) linewidth, of departure from crystallinity. In a polycrystalline sample the line intensity ratio of the doublet displayed in the presence of quadrupole splitting A_{12} averages to 1.0 when the angle between the principal axis of the electric field gradient and the direction of the gamma rays is distributed randomly. The departure from 1 is then an index of the degree of texture (or preferred crystal orientation). Finally the spectral area is a rough relative measure of the fraction of resonant atoms in the investigated surface layer, provided that all spectra are collected with the detector adjusted in the same conditions.

3. Results

Some typical CEMS spectra of tin oxide coated containers are presented in figure 1. All the spectra consist of unresolved doublets having isomer shift δ close to zero and quadrupole splitting Δ within the range 0.50 to

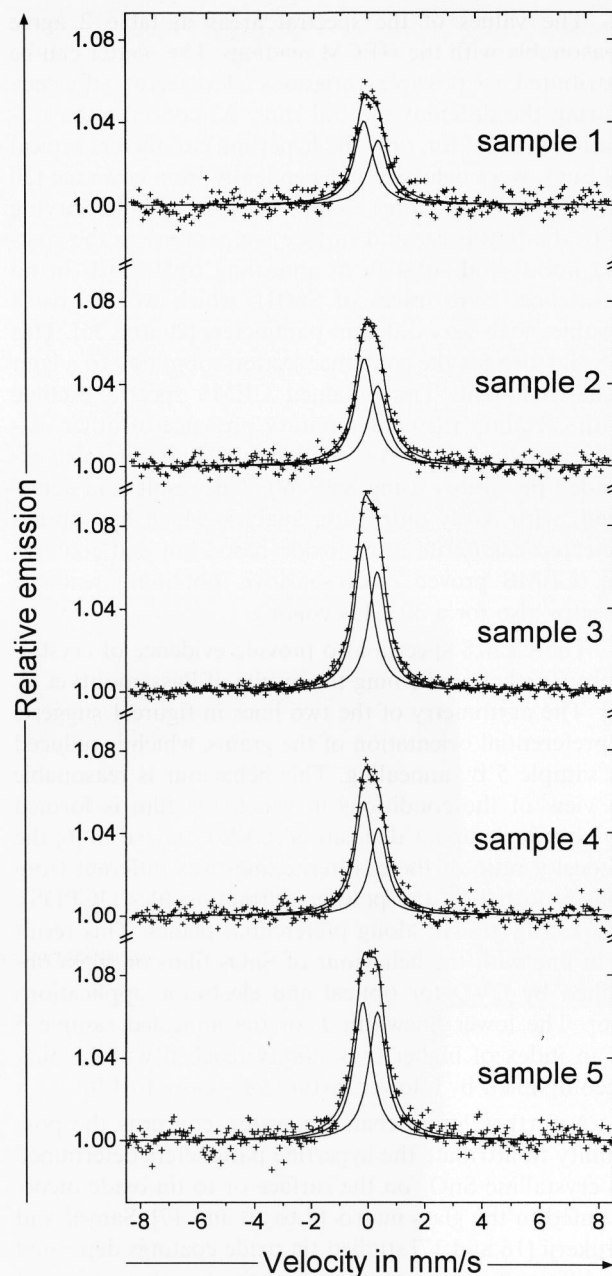


Figure 1. CEMS data and fit for samples 1 to 5. Crosses: experimental points, solid curves: data fit.

0.53 mm/s, suggesting that the structure of the surface film is crystalline, cassiterite-like [24]. In table 2 are reported the hyperfine parameters obtained using a current fitting procedure based on least squares minimization.

4. Discussion

Comparing the spectra in figure 1 and hyperfine parameters of as-received samples 1 to 4 with coverage ranging from 30 to 100 CTU, no significant differences were observed. The hyperfine parameters of the detected Sn(IV) doublets are quite uniform for samples 1 to 4 and allow the following considerations.

The values of the spectral areas in table 2 agree reasonably with the HECM readings. The scatter can be attributed to possible variations of detector efficiency during the different spectral runs. As concerns the oxidation state of tin, only the hyperfine parameters typical of SnO₂ were detected, independently from coverage (30 to 100 CTU), coating conditions (presumably varying with the bottle size and surface temperature in the coating hood) and subsequent annealing treatments. In no case there were traces of Sn(II), which would give a doublet with very different parameters [20 and 25]. This is valid also for the container section submitted to a later heat treatment. The obtained CEMS spectra exclude with certainty the contemporary presence of other oxidation states besides 4+, including metallic tin (also excluded previously using XPS [6]). This result is in agreement with X-ray diffraction analysis which had always detected cassiterite in tin oxide based hot end coatings [6]. CEMS proved more sensitive, obtaining readable spectra also for a 30 CTU coating.

The CEMS spectra also provide evidence of crystallinity, further confirming the results of Passamonti et al. [6]. The asymmetry of the two lines in figure 1 suggests a preferential orientation of the grains, which is reduced in sample 5 by annealing. This behaviour is reasonable in view of the conditions in which the film is formed by chemical vapour deposition (CVD). Indeed in [6] the intensity ratio of the cassiterite lines was different from that reported by the powder diffraction files (JCPDS), suggesting growth along preferential planes. This result is in line with the behaviour of SnO₂ films on glass obtained by CVD for optical and electronic applications [26]. The lower linewidth Γ of the annealed sample 5 is an index of higher crystallinity reached with heating accompanied by a lower texture (A_{12} close to 1.0).

A further long debated question concerns the possibility to attribute the hyperfine parameters determined to crystalline SnO₂ on the surface or to tin oxide incorporated in the glass matrix [8 to 10 and 17]. Sanyal and Mukerji [16 and 17] studied tin oxide coatings deposited at different temperatures and noticed a sharpening of

the whole tin spectrum, which they attributed to the diffusion of tin into the matrix with a change of coordination from tetragonal to octahedral. In table 2 the hyperfine parameters measured for hot end coatings are compared with those reported by the literature for crystalline cassiterite [26], for remelted float glass samples doped with up to 15 wt% tin oxide [27] and for tetravalent tin in the surface of float glass [20]. The differences recorded are not sensitive enough to differentiate the situations of SnO₂ forming a film on the glass surface versus those with SnO₂ dissolved in the glass matrix. However, the evidence of crystallinity found makes unlikely the hypothesis of tin dissolution in the matrix. The asymmetry of the Sn⁴⁺ doublet in figure 1 is quite evident, while the profiles of the Sn⁴⁺ peaks reproduced in [20, 25 and 27] are quite symmetric. Such results, in agreement with [6 and 18], contradict the model which describes the hot end coating process as an ion exchange process. Such model was based on earlier evidence – obtained with sequential HF attack – suggesting that tin oxide reacts with the glass matrix and migrates to considerable depths (of the order of 20 μ m) [8 and 10]. According to the experience of the present authors, the hypothesis of a significant tin interdiffusion was probably originated by the erratic dissolution of the coating, due to the fact that after HF attacks loosened tin oxide patches tend to adhere to the substrate [28]. The limited extent of interdiffusion gives experimental support to the discrete film model underlying both the optical treatment of the CTU readings and the mathematical elaboration of the microanalytical results outlined in [7].

5. Conclusions

The surface of tin oxide coated glass containers was analysed using Mössbauer spectroscopy in backscattering configuration (CEMS). The results demonstrate that CEMS can be used as a direct, simple and reliable method for the characterization of hot end coatings. The spectra are easily readable and can be quantitatively evaluated, giving indications on the tin content of the

Table 2. Hyperfine parameters obtained by fitting the experimental CEMS curves of samples 1 to 5. For comparison, the table also reports the values determined for crystalline cassiterite (CC) [26] and for tin dioxide in the glass matrix (TGM) [20 and 27].

sample no.	δ in mm/s	Δ in mm/s	Γ in mm/s	line intensity ratio A_{12}	spectral area
1	0.02	0.53	0.86	1.28	0.10
2	0.01	0.50	0.85	1.33	0.12
3	-0.02	0.51	0.80	1.23	0.16
4	0.01	0.53	0.81	1.31	0.12
5	-0.04	0.51	0.76	1.08	0.15
CC [26]	0.0	0.50	0.82		
TGM [20]	0.00 to 0.05	0.41 to 0.58	0.76 to 0.87		
TGM [27]	-0.20	0.42 to 0.48	0.85 to 0.94		

coating (related to the coating thickness), texture, and degree of crystallinity. In all the cases examined only tetravalent tin oxide in crystalline form with preferential orientation was present. No traces of tin in other oxidation states were observed. On annealing at 700°C a reduced grain orientation was detected. The consistent evidence of crystallinity excludes interdiffusion with the substrate.

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6. References

- [1] Geotti-Bianchini, F.; Preo, M.: Analysis of polyethylene-based cold end coatings on glass containers with contact angle and IR spectroscopy. *Glastech. Ber. Glass Sci. Technol.* **72** (1999) no. 11, p. 341–351.
- [2] Wasylyk, J. S.; Smay, G. L.: Parameters affecting the deposition of tin oxide onto glass surfaces and the function of tin oxide when overcoated with polyethylene in minimizing glass frictive damage. *Glastech. Ber.* **57** (1984) no. 9, p. 244–254.
- [3] Southwick, R. D.; Wasylyk, J. S.; Smay, G.L. et al.: The mechanical properties of films for the protection of glass surfaces. *Thin Solid Films* **77** (1981) p. 41–50.
- [4] Graham, P. W.: Lubricious and protective coatings for glass containers. *Ceram. Engin. Sci. Proc.* **7** (1986) no. 3–4, p. 439–459.
- [5] Cowan, N. D.; Benzing, P. C.; Budd, S. M.: Effect of surface treatment of glass containers on the release torque of pilferproof closures. *Glass Technol.* **20** (1979) no. 3, p. 86–88.
- [6] Passamonti, M. R.; Polzonetti, G.; Furlani, C. et al.: XPS, EPMA and XRD analysis of hot end coated glass containers. In: *Fundamentals of the glass manufacturing process 1991. Proc. 1st Conf. European Society of Glass Science and Technology, Sheffield 1991.* Sheffield: Society of Glass Technology, 1991. p. 22–27.
- [7] Geotti-Bianchini, F.; Verità, M.; De Riu, L. et al.: Evaluation of tin oxide coatings on glass containers using HECM and EPMA. *Glass Technol.* **35** (1994) no. 5, p. 216–223.
- [8] Rawson, H.; Turton, G.: The effect of coatings in reducing the damage of glass surfaces. *Glastech. Ber.* **46** (1973) no. 2, p. 28–33.
- [9] Budd, S. M.: ESCA examination of tin oxide coatings on glass surfaces. *J. Non-Cryst. Solids* **19** (1975) p. 55–64.
- [10] Korshunova, L. F.; Chitalov, A. N.; Kochetkova, G. V. et al.: Tin oxide coated container glasses. *Glass Ceram.* **47** (1990) no. 11, p. 431–433.
- [11] Fogelberg, C. V.; Romig, J. H.: Process for improved glass article coating, and such coated articles. US patent 4,289,816. Appl. date 3 Mar. 1980, publ. date 15 Sept. 1981.
- [12] Ali-Zaidi, S. R.: Process for forming rust resistant tin oxide coatings on glass containers. US patent 4,477,494. Appl. date 12 Jul. 1982, publ. date 16. Oct. 1984.
- [13] Wartenberg, E. W.: Method of coating glass. US patent 3,093,508. Appl. date 2 June 1960, publ. date 11 June 1963.
- [14] Geotti-Bianchini, F.; Scalet, B.; Verità, M.: SEM and X-ray microanalysis evaluation of tin oxide coatings on hollow glass. *Verres Réfr.* **35** (1981) no. 2, p. 245–248.
- [15] Bauer, A.; Žagar, L.: Verminderung der Kratzempfindlichkeit von Hohlgläsern durch Oberflächenbehandlung mit Zinnverbindungen. *Glastech. Berichte* **49** (1976) no. 3, p. 43–52.
- [16] Sanyal, A. S.; Mukerji, J.: A Mössbauer study of hot end coated tin on soda-lime glass. *Phys. Chem. Glasses* **26** (1985) no. 5, p. 135–136.
- [17] Mukerji, J.; Sanyal, A. S.: A Mössbauer spectroscopy study of the nature of the bond between glass, tin, and the organic molecule in hot and cold end coatings. *Phys. Chem. Glasses* **23** (1982) no. 3, p. 79–82.
- [18] Pantano, C. G.; Buyuklimanli, T.; Shallenberger, J. et al.: XPS and SIMS characterization of tin-oxide coatings on glass. *Glastech. Ber. Glass Sci. Technol.* **68 C1** (1995) p. 360–365.
- [19] Pantano, C. G.: Chemical and compositional analysis of glass surfaces. *Riv. Staz. Sper. Vetro* **20** (1990) no. 6, p. 123–135.
- [20] Principi, G.; Maddalena, A.; Gupta, A. et al.: Oxidation state of surface tin in an industrially produced float glass. *Nucl. Instr. Methods Phys. Res.* **B76** (1993) p. 215–217.
- [21] Meisel, W.: Depth profile of tin in float glass – a CEMS study. *Glastech. Ber. Glass Sci. Technol.* **72** (1999) no. 9, p. 291–294.
- [22] Williams, K. F. E.; Thomas, M. F.; Greengrass, J. et al.: The effect of tin on some physical properties of the bottom surface of float glass and the origin of bloom. *Glass Technol.* **40** (1999) no. 4, p. 103–107.
- [23] Gonser, U. (ed.): *Mössbauer spectroscopy.* Berlin et al.: Springer, 1975. (Topics in applied physics. Vol. 5.)
- [24] Principi, G.; Maddalena, A.; Gupta, A. et al.: CEMS characterization of SnO₂ films obtained by sputtering and sol-gel route. *Hyperfine Interactions* **69** (1991) p. 619–622.
- [25] Williams, K. F. E.; Johnson, C. E.; Greengrass, J. et al.: Tin oxidation state, depth profiles of Sn²⁺ and Sn⁴⁺ and oxygen diffusivity in float glass by Mössbauer spectroscopy. *J. Non-Cryst. Solids* **211** (1997) p. 164–172.
- [26] Caccavale, F.; Coppola, R.; Menelle, A. et al.: Characterisation of SnO_x films on architectural glass by neutron reflectometry, SIMS, CEMS and spectrophotometry. *J. Non-Cryst. Solids* **218** (1997) p. 291–295.
- [27] Johnson, J. A.; Johnson, C. E.; Williams, K. F. E. et al.: Mössbauer spectra of tin in float glass. *Hyperfine Interactions* **95** (1995) p. 41–51.
- [28] Scalet, B., Murano-Venice (Italy): Personal communication, 1999.

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