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^{57}Fe Hyperfine Parameters in Vitamins and Dietary Supplements

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Mössbauer (nuclear gamma-resonance) spectroscopy was used to study various industrial samples of vitamins and dietary supplements containing iron ions, which are used in the anemia treatment. Determination of the iron state (Fe^{2+} or Fe^{3+}) in medicaments is important for the pharmaceuticals evaluation quality. The investigated samples contain ferrous fumarate, ferrous gluconiate and ferric diphosphate. ^{57}Fe hyperfine parameters of the studied pharmaceuticals indicate that there exist major iron ferrous and ferric compounds. However, Mossbauer spectra of the investigated samples demonstrated the presence of additional ferrous and ferric components, probably related to impurities or to a partially modified main component.

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1. Introduction

Iron plays a very important role in the living systems. It is an integral part of many proteins and enzymes. Iron is also essential for the regulation of cell grown and differentiation. Iron deficiency causes anemia and other pathological changes in the body. Absorption of iron from food requires recognition of the chemical form of the iron by gut receptors. Both shape and charge are important in the recognition process. To be absorbed, dietary iron must be in its ferrous Fe^{2+} form, which is soluble, unless the Fe^{3+} ion is chelated (e.g., citrate, phytate, and heme) [1]. Therefore, the knowledge of the iron valence state is very important because it may be related to the effect and toxicity of pharmaceutical product.

Mössbauer spectroscopy is the most sensitive technique for the analysis of iron state [2, 3]. Hyperfine parameters of ^{57}Fe from Mössbauer spectra like isomer shift (Is) and quadrupole splitting (ΔE_q) give information about the iron electronic structure, valence and spin state of iron. These parameters may be used to characterize a quality of iron-containing pharmaceutical products. In this work we have studied ferrous and ferric iron containing vitamins and dietary supplements with the aim of analyzing the iron state and quality of these products.

2. Experimental procedure

Following samples of commercially available dietary supplements were chosen for this study: Prenatal Classic (Furitan's Pride Inc., USA), Biofer® (Cederroth International, Dania), ActiGlobin (Aflofarm, Poland) containing iron in the form of ferrous fumarate FeC_4H_{24}, Ascofer® (ESPEFA, Poland) containing ferrous gluconiate $Fe(C_6H_{11}O_7)_2{\cdot}H_20$ and Actiferol Fe® (Sequoia, UE) containing ferric diphosphate $Fe_4(P_2O_7)_3$. The studied dietary supplements containing different amount iron per one tablet: 60 mg in Prenatal Classic, 9 mg in Biofer®, 14 mg in Acti-Globin, 23.2 mg in Ascofer® and 7 mg in Actiferol Fe®. The Mössbauer investigation was made on powdered samples.

The ^{57}Fe Mössbauer spectra were recorded at room temperature with a constant acceleration spectrometer with ^{57}Co:Cr source, a multichannel analyzer with 1024 channels, and linear arrangement of the ^{57}Co source, absorber and detector. The spectrometer velocity was calibrated with a high purity α-Fe foil. The values of isomer shifts (Is) for all identified subspectra were determined relatively to the α-Fe standard. The obtained spectra were fitted as a superposition of several doublets.

3. Result and discussion

The room temperature Mössbauer spectrum of dietary supplements containing ferrous fumarate are presented in Figure 1. The fitting parameters of all the Mössbauer spectra are listed in Table. The Mössbauer hyperfine parameters corresponding to $FeC_4H_2O_4$ were the same within the error and match these presented in literature [2, 4]. However, additional components connected with Fe^{3+} ions are visible on these spectra. The existence of Fe^{3+} ions may be considered as an impurity or a result of ferrous fumarate oxidation and formation of ferric fumarate as it was supposed in [4].

The Mössbauer spectrum of Ascofer® containing the ferrous gluconate is presented in Figure 2. This spectrum was fitted by tree doublets. The parameters of the two of them (Table) are connected with $Fe(C_6H_{11}O_7)_2H_2O$ [9, 10]. However, these duplets have different values of quadrupole splitting ΔE_q, which suggests that Fe^{2+} ions occupy two different iron sites with slightly different symmetry. The hyperfine parameters of third doublet indicated on existing in Ascofer® also

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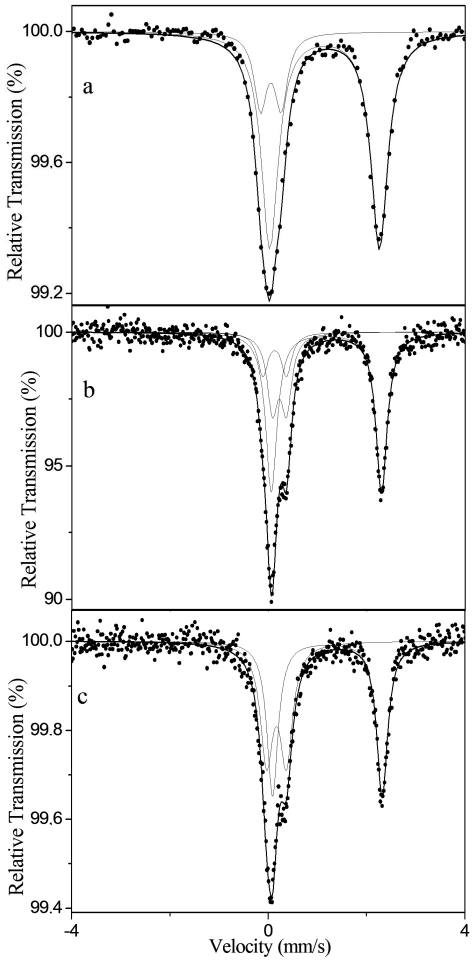

Fig. 1. The room temperature ^{57}Fe Mössbauer spectrum of dietary supplements containing ferrous fumarate: a — Prenatal Classic, b — Acti-Globin, c — Biofer®. The fitted subspectra are presented on the spectrum.

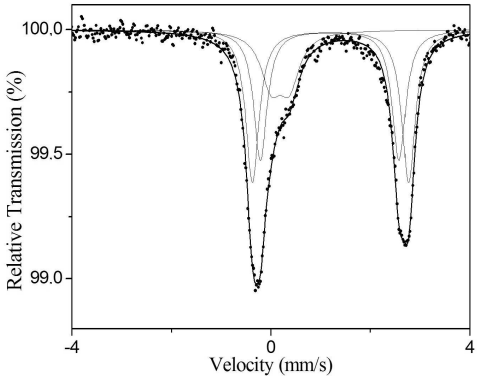

Fig. 2. The room temperature ^{57}Fe Mössbauer spectra of Ascofer® containing ferrous gluconiate. The fitted subspectra are presented on the spectrum.

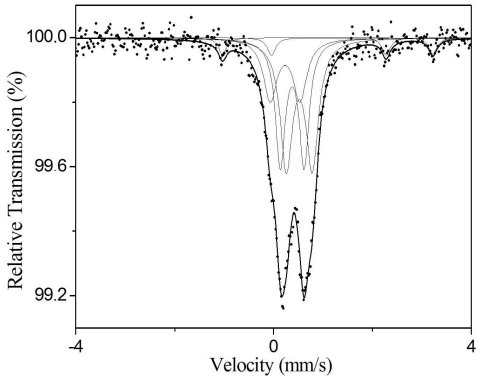

Fig. 3. The ^{57}Fe Mössbauer spectra of Actiferol Fe® containing ferric diphosphate recorded at room temperature. The fitted subspectra are presented on the spectrum.

TABLE I

The ^{57}Fe Mössbauer hyperfine parameters of the investigated pharmaceuticals: isomer shift Is, quadrupole splitting ΔE_q, intensity A. Experimental errors are smaller than 6%.

Sample	Is [mm/s]	ΔE_q [mm/s]	A [%]	Compound
Prenatal	1.19	2.23	80	Ferrous fumarate
Classic	0.10	0.42	20	Ferric high spin
Acti-Globin	1.20	2.22	60	Ferrous fumarate
	0.24	0.28	26	Ferric high spin
	0.14	0.48	14	Ferric high spin
Biofer®	1.22	2.22	54	Ferrous fumarate
	0.18	0.49	46	Ferric high spin
Ascofer®	1.22	3.13	42	Ferrous gluconiate
	1.20	2.78	36	Ferrous gluconiate
	0.21	0.36	22	Ferric high spin
Actiferol Fe®	0.26	0.50	21	Ferric diphosphate
	0.40	0.48	11	$\beta-Fe_3(P_2O_7)_2$
	1.11	4.26	3	
	0.54	0.52	40	$\alpha-Fe_3(P_2O_7)_2$
	1.14	2.32	3	$Fe_2P_2O_7$

Fe^{3+} ions. These ions are probably an integral part of the ferrous gluconate structure [6, 7].

The Mössbauer spectrum of ferric diphosphate recorded at room temperature is shown on Figure 3. It was fitted with five doublets. The Mössbauer parameters of these doublets are given in Table. Two of them are connected with Fe^{2+} ions ($\approx$ 7%) and the others with Fe^{3+} ions. The identification of compounds connected with these ions was not very easy. We may suppose that the doublet with Is and ΔE_q values 0.26 mm/s and 0.50 mm/s is attributed to $Fe_4(P_2O_7)_3$. The doublet with Is and ΔE_q values 1.14 mm/s and 2.32 mm/s is probably connected with $Fe_2P_2O_7$ [8, 9]. Two doublets with Is and ΔE_q values of 0.40 mm/s and 1.11 mm/s, and 0.48 mm/s and 4.32 mm/s, respectively, could be attributed to the $\beta-Fe_3(P_2O_7)_2$ [9]. The last doublet on the Mössbauer spectrum of Actiferol Fe® with hyperfine parameters isomer shift 0.54 mm/s and quadrupole splitting 0.52mm/s is connected with $\alpha-Fe_3(P_2O_7)_2$ [9].

4. Conclusions

The results of the applications of the Mössbauer spectroscopy to study various industrial samples of vitamins and dietary supplements containing iron ions demonstrate wide possibilities of this technique. ^{57}Fe hyperfine parameters of the studied pharmaceuticals indicate on the existence of major iron ferrous and ferric compounds. The investigated dietary supplements with the ferrous fumarate contain from about 54% to 80% of these compounds. The supplements with ferrous gluconiate have about 78% of major phase. In Actiferol Fe®, the ferric diphosphate is only about 21%. The obtained Mössbauer spectra indicated on the presence of additional ferrous and ferric compounds, with different relative contribution, probably related to impurities or to partially modified main components. Also, the additional ferric compounds in medicaments containing ferrous fumarate and gluconiate could be due to using preservatives with iron.

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