

The Oxidation of Magnetic Particles in Medicinal Ointment

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Magnetic particles in a novel, wound-healing ointment were studied using Mössbauer spectroscopy and VSM to estimate the stability of the properties of the magnetic particles. The isomer shifts of $\text{Fe}_3\text{O}_4(\text{A})$ were found to be 0.49-0.56 mm/s relative to iron metal, this indicates that the iron ions in $\text{Fe}_3\text{O}_4(\text{A})$ are Fe^{3+} . On the other hand, the isomer shifts of $\text{Fe}_3\text{O}_4(\text{B})$ were found to be 0.91-1.13 mm/s relative to iron metal, this shows that the ion state of $\text{Fe}_3\text{O}_4(\text{B})$ is a mixed state of Fe^{2+} and Fe^{3+} . It is noted that this composition, as well as that of the initial pure component in the form of a highly dispersed fraction ($\sim 10 \text{ \AA}$), differs from the stoichiometric one. It was found that the area ratio of the Mössbauer subspectra of $\text{Fe}_3\text{O}_4(\text{A}) / \text{Fe}_3\text{O}_4(\text{B})$ taken at 87 and 181 K linearly increased in comparison to the initial pure magnetic particles, but the rate of increase of the area ratio at 181 K was about two times that at 87 K. From the magnetic hyperfine field, despite their small size, the particles exhibit no superparamagnetism.

Keywords : Mössbauer spectroscopy, magnetic particle, drug, oxidation

1. Introduction

Recently, many novel, multipurpose drugs that contain remarkable concentrations of iron have appeared [1]. In the case of iron-containing medicinal drugs, Mössbauer spectroscopy can be used for the determination of both the iron valency and the control of stability. It is very important that the application of any new drugs on a wide scale undergoes not only exact testing but also development of their contents for standardization and quality criteria. Concrete research methods are determined according to the composition of a drug and physicochemical properties of its bases. Mössbauer spectroscopy has not been widely applied to medical problems, such as searching for new approaches to improve the efficiency of drugs, until now. However, it seems that this method is unique for testing medicinal composites since it simultaneously gives us information about both the local peculiarities of the substance being studied and its macroscopic properties. Recently, a new, multipurpose wound-healing ointment was synthesized. It was found that the magnetic particles in the ointment enhanced its medical effect. The purpose of this study is to carry out Mössbauer and magnetic susceptibility measurements on the new wound-healing

ointment to estimate the properties and composition stability of its magnetic component.

2. Experimental

The vaseline-lanoline-based magnetic wound-healing ointment with highly dispersed magnetite particles synthesized by Elmar's method was studied [1]. Mössbauer spectroscopy is well suited to be the main tool for non-destructive investigation since the magnetic component of the ointment contains Fe. Magnetic susceptibility was measured using a vibration sample magnetometer (VSM). A Mössbauer spectrometer of the electromechanical type was used with a 512-channel analyzer in the constant-acceleration mode. A 20 mCi ^{57}Co source in a rhodium matrix was used at room temperature [2]. The spectrometer was calibrated using standard absorbed sodium nitroprusside $\text{Na}_2\text{Fe}[\text{CN}_5\text{NO}]\cdot 2\text{H}_2\text{O}$. To ensure fine enough samples we set the absorber thickness to 0.2 mg $^{57}\text{Fe}/\text{cm}^2$. Mössbauer spectra were taken at various temperatures from liquid nitrogen to room temperature.

3. Result and Discussion

Three kinds of samples were prepared with Fe_3O_4 and Fe_2O_3 magnetic particles. The initial pure magnetic particles, in the form of a highly dispersed fraction ($\sim 10 \text{ \AA}$), were

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fabricated. The samples initially consisted of pure magnetic particles (sample 1), magnetic paste concentrate (sample 2), and magnetic paste concentrate with medicinal additions (sample 3). Mössbauer spectra of all samples were taken at various temperatures ranging from liquid nitrogen to room temperature. Using a least-squares computer program, three sets of six Lorentzian-lines corresponding to the $Fe_3O_4(A)$, $Fe_3O_4(B)$ and Fe_2O_3 were fitted to the Mössbauer spectra below the Néel temperature under well-known restraints, these are valid when the quadrupole interaction is much weaker than the magnetic hyperfine interaction [3].

Figure 1 shows the Mössbauer spectra of magnetic particles of the paste concentrate at 87 K and 181 K. It can be seen that with increasing temperature from 87 to 181 K the subspectrum intensity of $Fe_3O_4(A)$ increases, while that of $Fe_3O_4(B)$ decreases. The refined Mössbauer parameters for sample 1, 2 and 3 are shown in Table 1. The respective areas of the subspectrum of Fe_2O_3 are not changed with temperature variation. In Table 1, the isomer shifts of $Fe_3O_4(A)$ were found to be 0.49-0.56 mm/s relative to iron metal, this indicates that the iron ions in $Fe_3O_4(A)$ are Fe^{3+} [4].

The magnitudes of the magnetic fields shown in Table 1 also show the ferric character of the Fe ions in $Fe_3O_4(A)$. On the other hand, the isomer shifts of $Fe_3O_4(B)$ were

Table 1. Mössbauer parameters for magnetic particles in medicinal ointment at 87 K. H_f is the magnetic hyperfine field, ΔE_Q is the quadrupole splitting and δ is the isomer shift relative to metallic iron at room temperature.

Samples	Subspectrum	H_f (kOe)	E_Q (mm/sec)	δ (mm/sec)
1	$Fe_3O_4(A)$	494 ± 1	0.03 ± 1	0.49 ± 3
	$Fe_3O_4(B)$	466 ± 5	0.05 ± 3	0.91 ± 8
	Fe_2O_3	500 ± 1	0.01 ± 3	0.71 ± 1
2	$Fe_3O_4(A)$	497 ± 1	0.04 ± 3	0.57 ± 3
	$Fe_3O_4(B)$	445 ± 5	0.05 ± 2	0.99 ± 8
	Fe_2O_3	501 ± 1	0.05 ± 1	0.69 ± 3
3	$Fe_3O_4(A)$	499 ± 1	0.03 ± 2	0.56 ± 3
	$Fe_3O_4(B)$	458 ± 5	0.12 ± 5	1.13 ± 5
	Fe_2O_3	501 ± 1	0.08 ± 2	0.70 ± 3

found to be 0.91-1.13 mm/s relative to iron metal, this shows that the ion state of $Fe_3O_4(B)$ is a mixed state of Fe^{2+} and Fe^{3+} [5]. Fe_3O_4 (magnetite) has a so-called inverse spinel structure, with Fe^{3+} ions on the tetrahedral sites (A-site) and the rest on octahedral sites (B-site) [6, 7]. The cation distribution of iron, however, is known to be changed by heat treatment [8]. Figure 2 shows the area ratio of the Mössbauer subspectra of $Fe_3O_4(A)/Fe_3O_4(B)$ at the temperature of 87 K for sample 2. The area ratio of the Mössbauer subspectra of $Fe_3O_4(A)/Fe_3O_4(B)$ for sample 2 at 181 K is shown in Fig.3.

It was found that the area ratio of the Mössbauer subspectra of $Fe_3O_4(A)/Fe_3O_4(B)$ taken at 87 and 181 K linearly increased in comparison to the initial pure magnetic particles (sample 1), but the rate of increase of the area ratio at 181 K is about two times that at 87 K. This suggests the oxidation of magnetic particles. The change

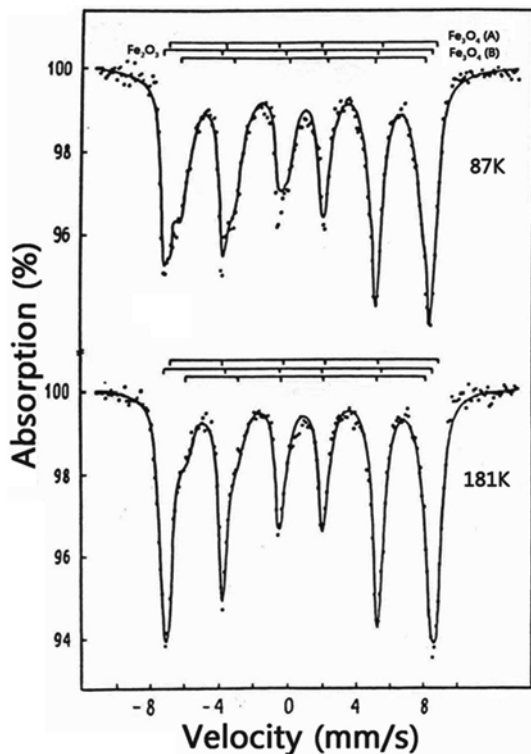


Fig. 1. Mössbauer spectra of magnetic particles of the paste concentrate at 87 and 181 K.

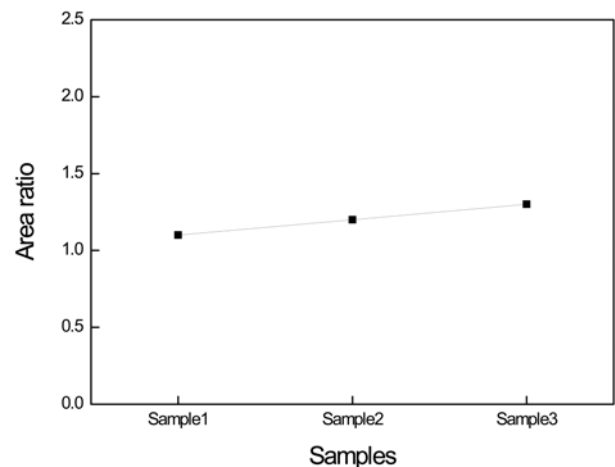


Fig. 2. The area ratio of Mössbauer subspectra $Fe_3O_4(B)/Fe_3O_4(A)$ taken at 87 K.

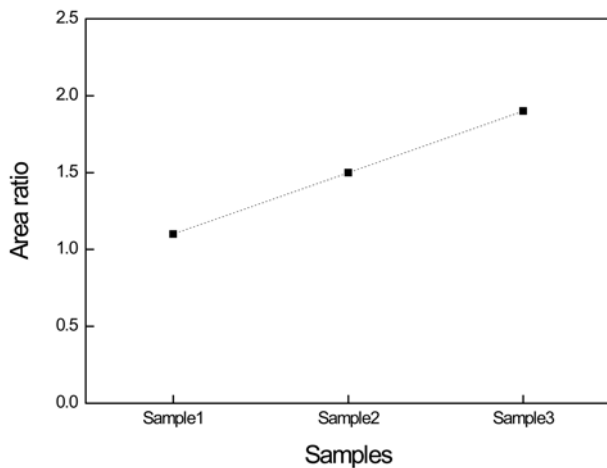


Fig. 3. The area ratio of Mössbauer subspectra $\text{Fe}_3\text{O}_4(\text{B})/\text{Fe}_3\text{O}_4(\text{A})$ taken at 181 K.

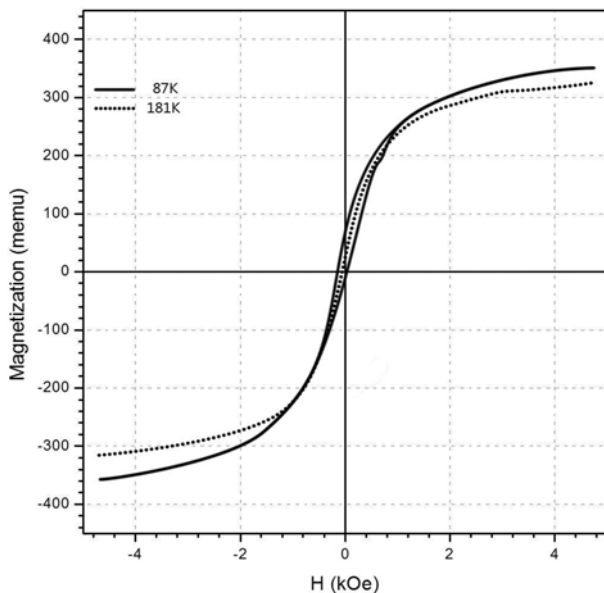


Fig. 4. Hysteresis loops of the magnetic component particles in the paste concentrate.

from stoichiometry is a result of the oxidation of magnetic particles during both synthesis and storage. Use of the magnetic particles as the base for the magnetic particles concentrate results in additional oxidation. It is noteworthy that storage affects the magnetic particles' oxidation more than synthesis.

Figure 4 shows VSM measurements. It was found that

the particles exhibit practically no superparamagnetism despite their small size, this may be explained by the small particles joining together into conglomerates when synthesizing the ointment [9].

4. Conclusion

Three kinds of samples, initial pure magnetic particles (sample 1), magnetic paste concentrate (sample 2) and magnetic paste concentrate with medicinal additions (sample 3) were studied by Mössbauer spectroscopy and VSM to estimate the stability of the properties of the magnetic particles. The deviation from stoichiometry is due to the oxidation of magnetic particles during both synthesis and storage. Use of the magnetic particles as the base for the magnetic particles concentrate also results in additional oxidation. It is noteworthy that storage affects the magnetic particles' oxidation more than synthesis. It was found that the particles exhibit practically no superparamagnetism despite their small size, this may be explained by the small particles joining together into conglomerates when synthesizing the ointment.

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References

- [1] A. V. Bykov, V. I. Nikolaev, and V. S. Rusakov, *Moscow Univ. Phys. Bull.* **42**, 116 (1987).
- [2] H. N. Ok, Y. Chung, and J. G. Kim, *Phys. Rev. B* **20**, 4550 (1979).
- [3] G. A. Sawatzky, F. van der Woude, and A. H. Morrish, *Phys. Rev.* **187**, 747 (1969).
- [4] S. W. Lee, S. H. Yoon, S. Y. An, and W. C. Kim, *J. Magnetism* **4**, 115 (1999).
- [5] W. C. Kim, S. J. Kim, and C. S. Kim, *J. Magn. Magn. Mater.* **239**, 82 (2002).
- [6] D. S. McClure, *J. Phys. Chem. Solids.* **3**, 311 (1957).
- [7] G. D. Rieck and J. J. Thijssen, *Acta Crystallogr. Sect. B* **24**, 982 (1978).
- [8] H. N. Ok and Y. K. Kim, *Phys. Rev. B* **36**, 5120 (1987).
- [9] H. N. Ok and M. S. Han, *J. Appl. Phys.* **44**, 1932 (1973).