Mössbauer effect in amorphous media

Authors: K.V. Antokhina[1], A.I. Velichkov[1,2], D.V. Karaivanov[1,2], A. Baimuhanova[1,3], N.Temerbulatova[1,3], S.P. Kubrin[4], D.A. Sarychev[4], V.M. Vahtel[5], U.G. Semov[5], D.V. Filosofov[1]

[1]*Joint Institute for Nuclear Research, Dubna, Russia*
[2]*The Institute for Nuclear Research and Nuclear Energy of the Bulgarian Academy of Sciences, Sofia, Bulgaria*
[3]*Institute of Nuclear Physics, Almaty, Kazakhstan*
[4]*Southern Federal University, Rostov-on-Don, Russia*
[5]*Voronezh State University, Voronezh, Russia*

Goals and objectives

Goals: determination of ionic forms of iron in ion exchange resin by nuclear gamma resonance

Objectives:

- Preparing the samples of resins washing in solutions of salt of iron
- Measuring samples on the Mössbauer spectrometer
- Analysis of spectra of samples

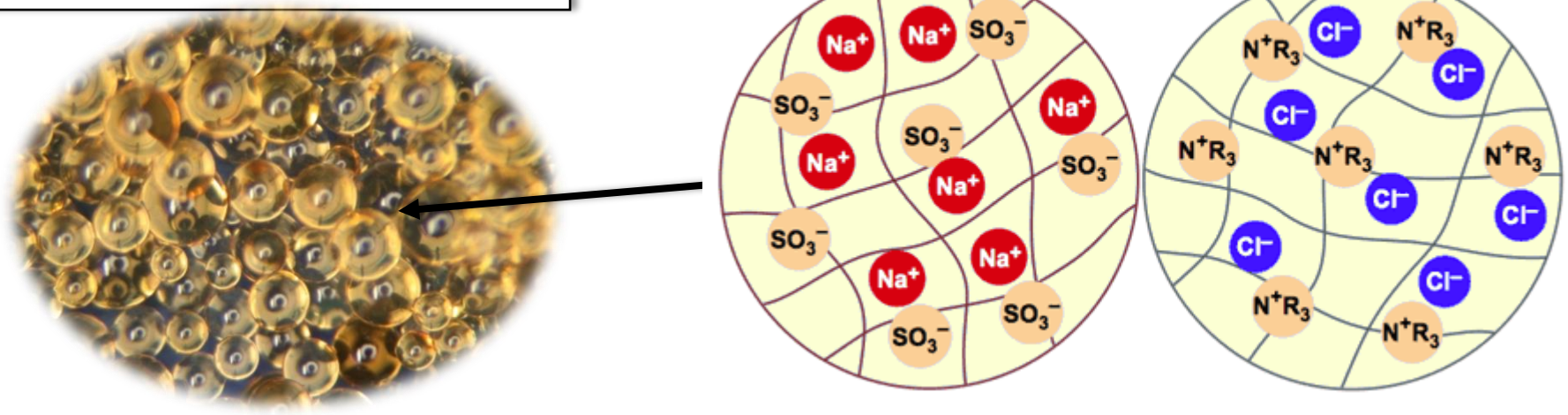
Ion exchange resin

Ion exchangers are gel-like dispersed systems. Any ion exchanger consists of a matrix and functional groups capable of ion exchange. Most modern ion exchangers have a framework made of styrene-divinylbenzene copolymer, which is an elastic hydrocarbon three-dimensional network. In a sense, ion exchange resins can be considered a solid, but without strict periodicity.

$$\overline{nR - SO_3^- \, {}^1Me^{n+}(H_2O)_k} + {}^2Me^{m+}(H_2O)_k \leftrightarrows \overline{mR - SO_3^- \, {}^2Me^{m+}(H_2O)_k} + {}^1Me^{n+}(H_2O)_k$$

$\overline{nR - SO_3^- \, {}^1Me^{n+}(H_2O)_k}$ & $\overline{mR - SO_3^- \, {}^2Me^{m+}(H_2O)_k}$ – ions on the resin,

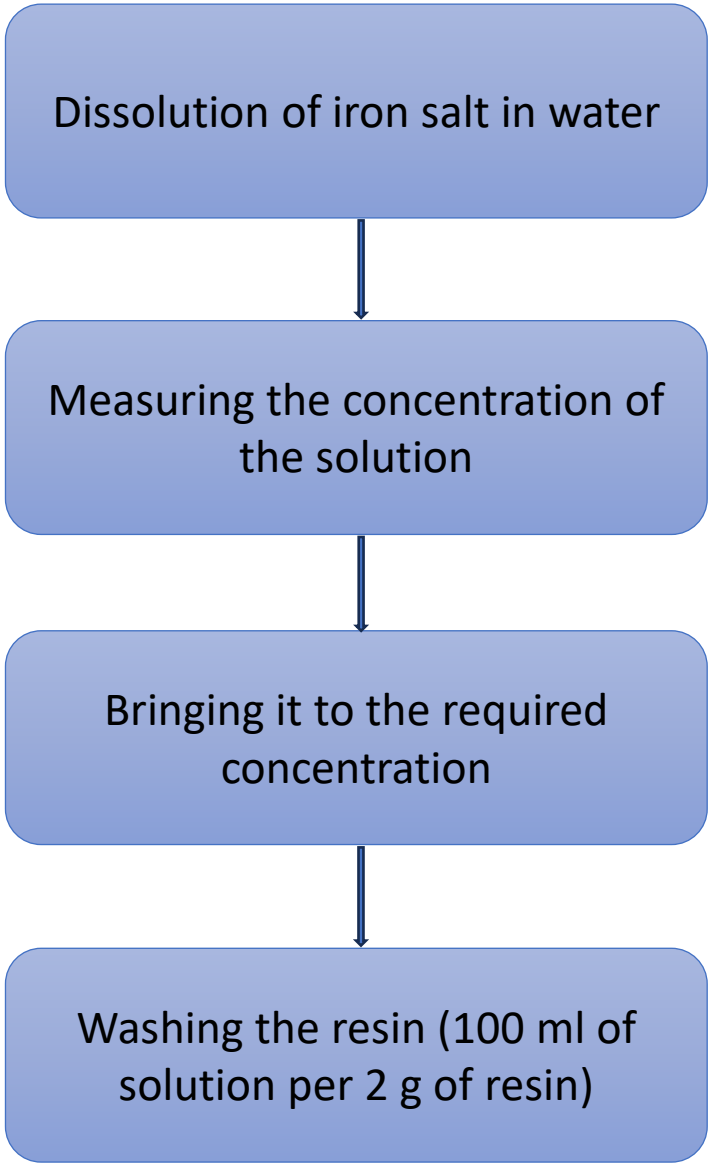
${}^2Me^{m+}(H_2O)_k$ & ${}^1Me^{n+}(H_2O)_k$ – ions in the solution.



Preparing of samples

Table 1. Conditions for sample preparation

	Resin	Solution	Masses of resin, g	Volume of solution, ml
N1	Dowex 50WX8 (200-400 mesh)	0.1M $FeCl_3$	6	300
N2		0.1M $FeCl_3$ + 1M HCl	4	200
N3		0.1M $Fe(NO_3)_3$	10	500
N4		0.1M $Fe(NO_3)_3$ + 0.3M HNO_3	4	200
N5		0.1M $Fe(NO_3)_3$ + 1M HNO_3	4	200
N6		0.1M $Fe(NO_3)_3$ + 3M HNO_3	4	200
N7		0.1M $FeSO_4$	4	200
N8	Dowex 1X8 (100-200 mesh)	0.1M $FeCl_3$+6M HCl	4	200



Method of Mössbauer spectroscopy

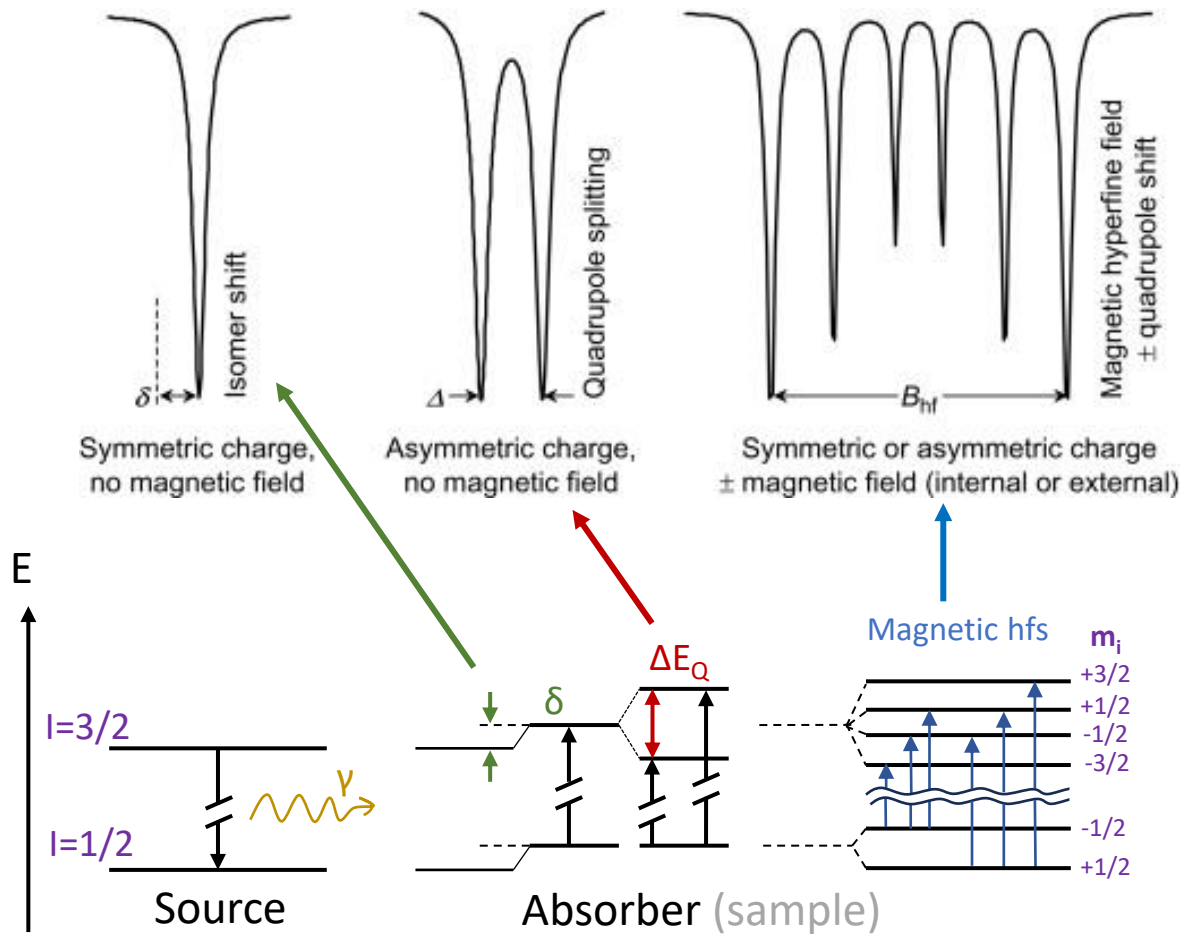


Fig. 1. Mössbauer spectra of Fe^{57} and scheme of energy levels of (a) isomeric shift, (b) quadrupole splitting and (c) superfine magnetic splitting

Fig. 2. MC1104Em express Mössbauer spectrometer (top) and low-temperature Mössbauer complex (bottom)

Predominance diagram

The predominace diagrams show the equilibrium of ions and their complexes in solution depending on the concentration of the anion.

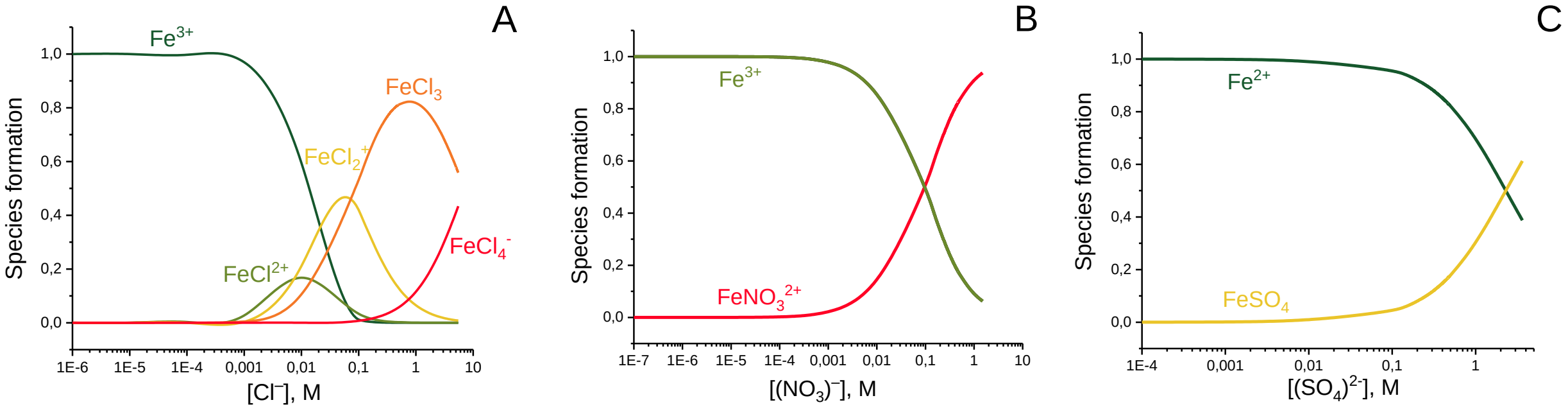


Fig. 3. Species of iron in the solution of (a) $FeCl_3$, (b) $Fe(NO_3)_3$ and (c) $FeSO_4$

Results and discussion: Mössbauer spectra of cation exchanger washed in solution of $FeCl_3$

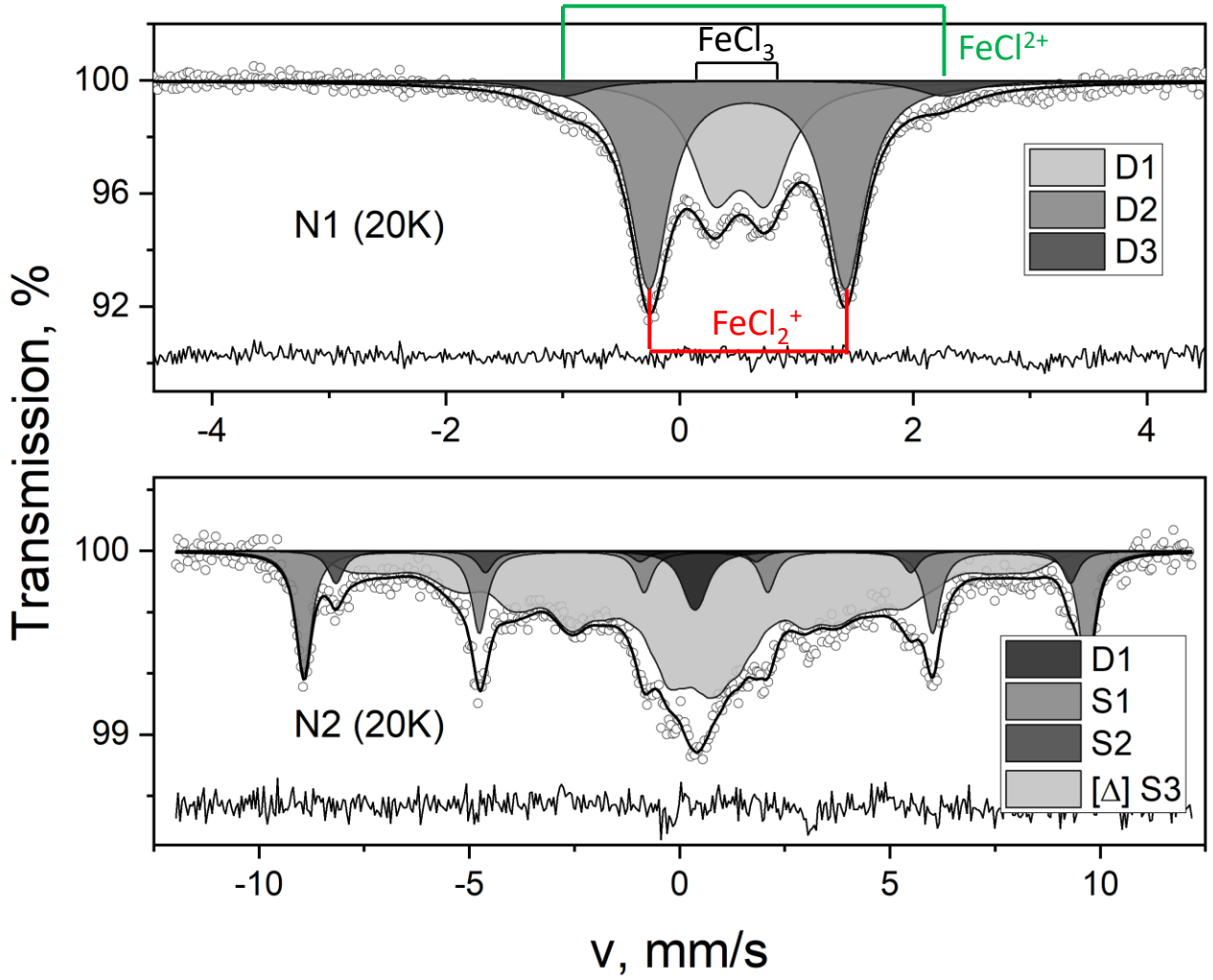


Table 2. Mössbauer parameters of samples of Dowex 50WX8 washed in solutions of $FeCl_3$ (fig. 4).

Sample	Components	Is±0.01, mm/s	Qs±0.01, mm/s	H±1, kOe	Γ±0.01, mm/s	A±1, %	χ^2
N1 (20K)	D1	0.52	0.44		0.47	34.6	1.190
	D2	0.58	1.68		0.41	58.1	
	D3	0.64	3.26		0.60	6.5	
N2 (20K)	D1	0.37	0.22		0.60	4.0	1.228
	S1	0.50	-0.26	577	0.45	22.3	
	S2	0.50	0.12	542	0.45	5.9	
	[Δ]S3	0.41	-0.30	560	0.30	67.8	

Is – isomer shift, Qs – quadrupole splitting, Γ – line width, A – area of the component (portion of form), χ^2 – Pearson's chi-squared test, D – doublet, S – sextet, [Δ] – distribution.

Fig. 4. Mössbauer spectra of cation exchanger Dowex 50WX8 washed in solutions: *N1* – 0.1M $FeCl_3$; *N2* – 0.1M $FeCl_3$ + 1M HCl

Results and discussion: Mössbauer spectra of cation exchanger washed in solution of $Fe(NO_3)_3$

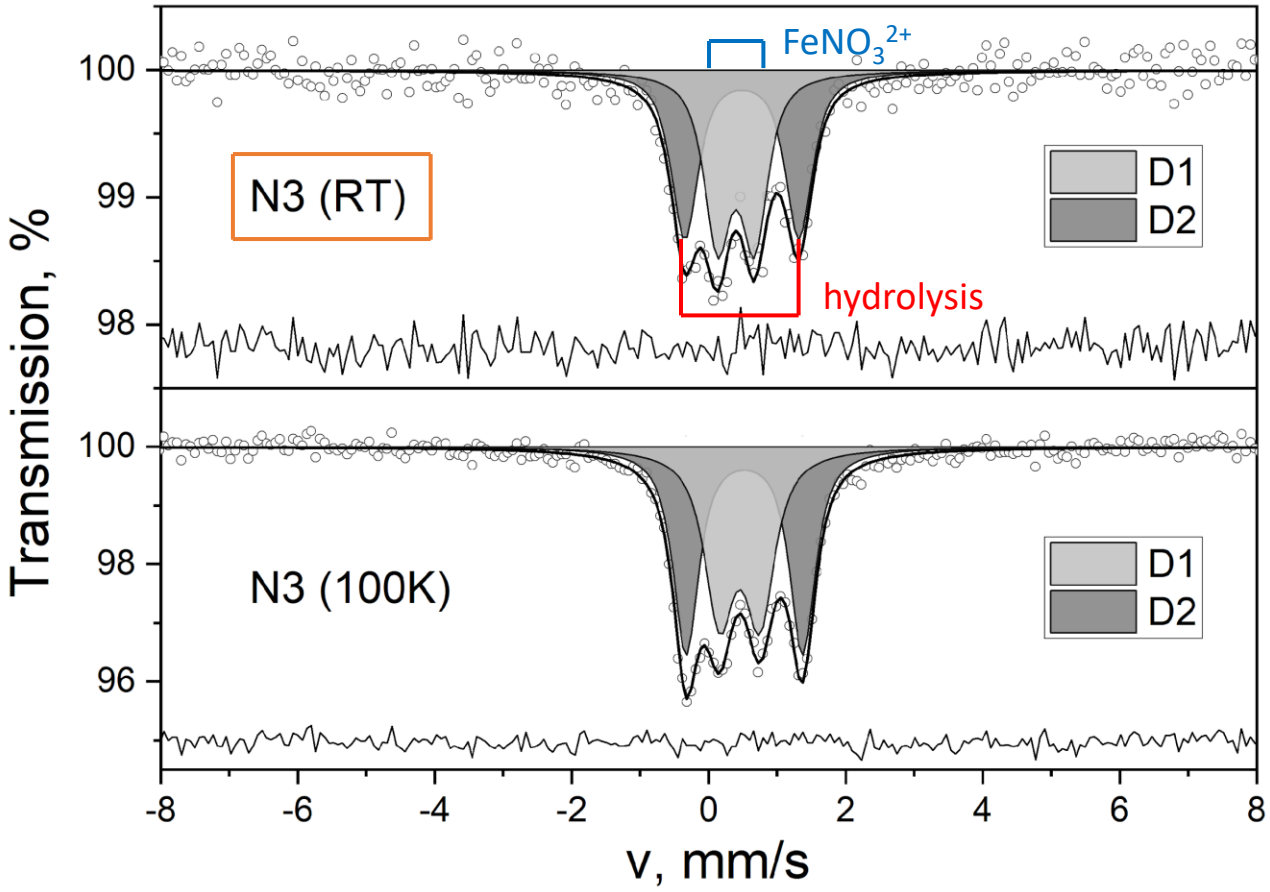


Fig. 5. Mössbauer spectra of cation exchanger Dowex 50WX8 washed in solution: *N3* – 0.1M $Fe(NO_3)_3$

Table 3. Mössbauer parameters of samples of Dowex 50WX8 washed in solutions of $Fe(NO_3)_3$ (fig. 5).

Sample	Components	Is±0.01, mm/s	Qs±0.01, mm/s	H±1, kOe	Γ±0.01, mm/s	A±1, %	χ^2
N3 (RT)	D1	0.40	0.54		0.46	49	1.097
	D2	0.48	1.66		0.47	51	
N3 (100K)	D1	0.45	0.58		0.46	49	1.097
	D2	0.52	1.71		0.47	51	

Results and discussion: Mössbauer spectra of cation exchanger washed in solution of $FeSO_4$

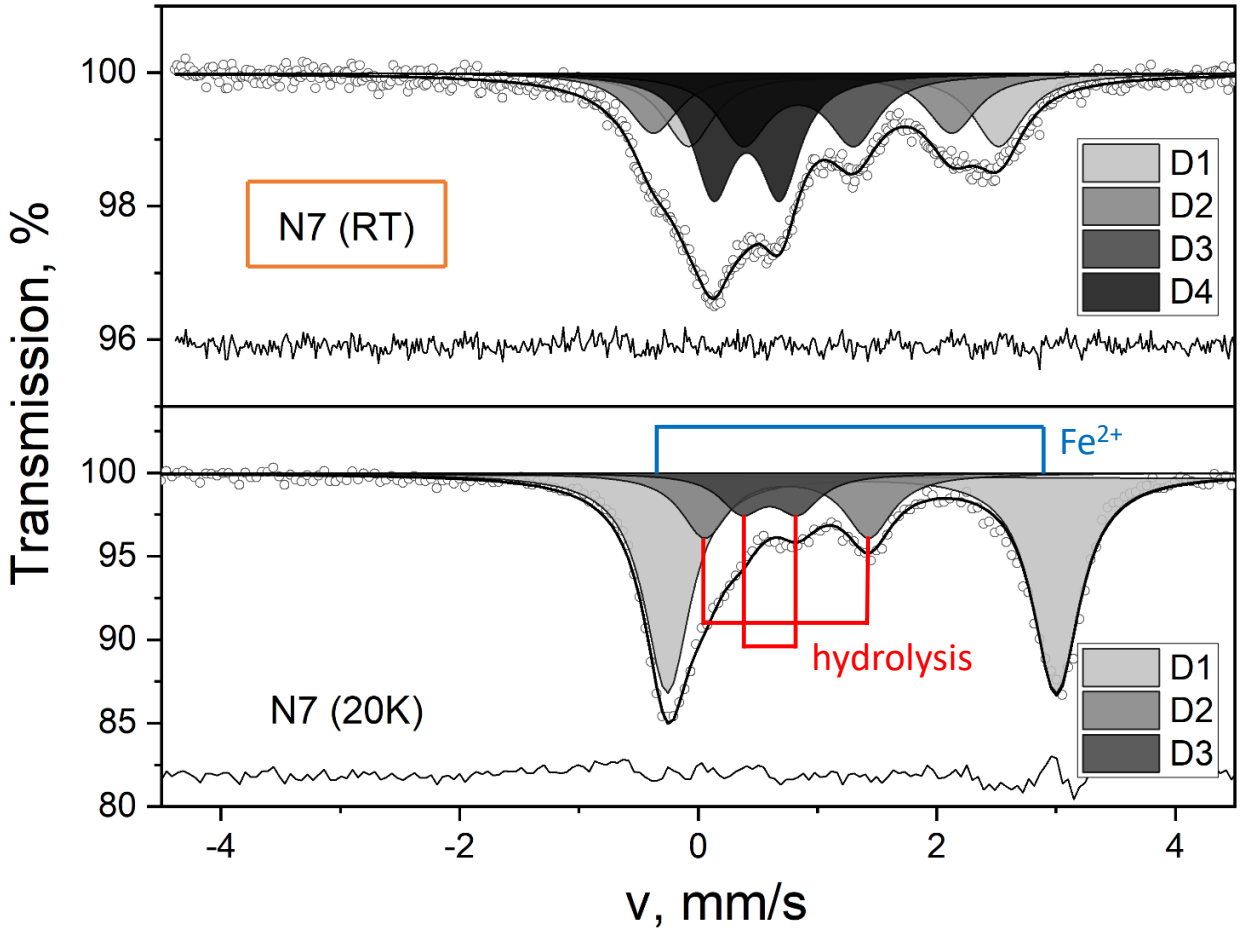


Fig. 6. Mössbauer spectra of cation exchanger Dowex 50WX8 washed in solution: *N7* – 0.1M $FeSO_4$

Table 4. Mössbauer parameters of samples of Dowex 50WX8 washed in solutions of $Fe(NO_3)_3$ (fig. 6).

Sample	Components	Is±0.01, мм/с	Qs±0.01, мм/с	Γ±0.01, мм/с	A±1, %	χ^2
N7 (RT)	D1	1.22	2.60	0.52	25.0	1.120
	D2	0.87	2.50	0.52	20.5	
	D3	0.84	0.92	0.51	23.4	
	D4	0.41	0.56	0.41	31.1	
N7 (20K)	D1	1.37	3.26	0.47	68.8	1.959
	D2	0.74	1.38	0.48	20.4	
	D3	0.60	0.48	0.44	10.8	

Diffusion coefficients

Table 5. Diffusion coefficients ions in strong acid cation exchangers.		
Cation	Ion exchanger	D_r, см^2/с
H^+	Dowex 50-X8	$5.40 \cdot 10^{-6}$
Na^+	Dowex 50-X8	$2.88 \cdot 10^{-7}$
Sr^{2+}	Dowex 50-X8	$3.38 \cdot 10^{-8}$
Y^{3+}	Dowex 50-X8	$3.18 \cdot 10^{-9}$

Conclusion

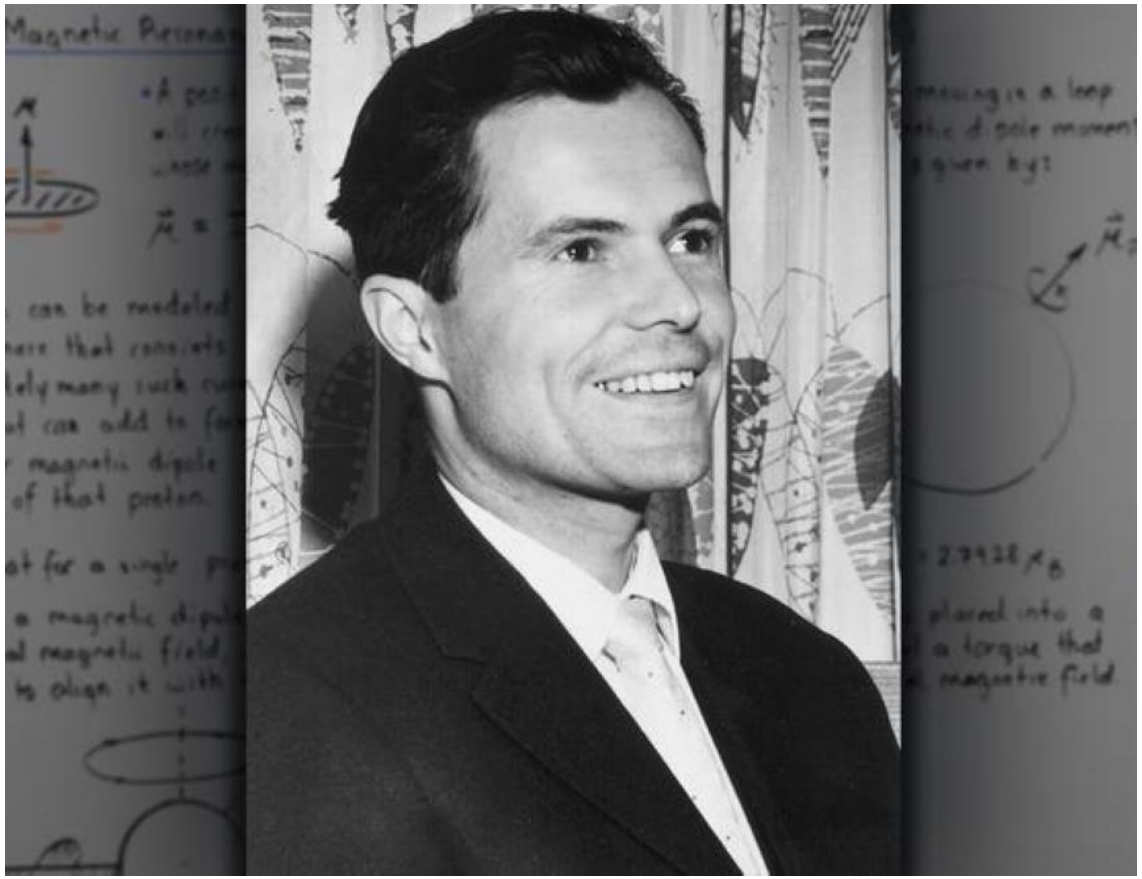
Mössbauer spectra of ion exchange resins washed in solutions of different iron salts ($FeCl_3$, $Fe(NO_3)_3$, $FeSO_4$) were obtained. According to the results obtained, it can be concluded that the nuclear gamma resonance method is suitable for studies of ion-exchange resins, and the method can give information about the forms of iron in the resin. Thus, the following results were obtained during the experiments:

- The ionic forms are observed in Dowex 50WX8 ion exchange resin washed in iron (III) chloride solutions: $Fe(H_2O)_3Cl_3$, $Fe(H_2O)_4Cl_2^+$, $Fe(H_2O)_4Cl^{2+}$, $Fe(OH)Cl^+$. With increasing pH, it is possible to observe the form $Fe(H_2O)_2Cl_4^-$;
- in Dowex 1X8 ion exchange resin washed in strongly acidic ferric chloride solution, the following forms are observed: $Fe(H_2O)_2Cl_4^-$, $Fe(H_2O)_3Cl_3$;
- in Dowex 50WX8 resin washed in iron (II) nitrate solutions, the form $Fe(H_2O)_5NO_3^{2+}$ as well as hydrolysis products are observed;
- in Dowex 50WX8 resin washed in iron (II) sulfate solutions, the forms Fe^{2+}, $Fe(H_2O)_4(SO_4)_2^-$ are observed;
- the observation of the effect at room temperature is also an important result. Probably, the possibility of performing experiments at room temperature is due to the mobility of the ions. Measurements of cationite washed in iron (III) chloride solutions failed due to the formation of multi-ligand complexes, with lower total positive charge, which increases mobility and makes it difficult to obtain Mössbauer spectra.

References

- Helfferich, Friedrich G. Ion exchange. Courier Corporation, 1995.
- Marhol, Milan. "Ion exchangers in analytical chemistry, their properties and use in inorganic chemistry." Comprehensive analytical chemistry 14 (1982).
- Лурье, Юлий Юльевич. Справочник по аналитической химии. Рипол Классик, 2013.
- Wertheim, Gunther K. Mössbauer effect: principles and applications. Academic Press, 2013.

Thank you for your attention!



Backup

Results and discussion: Mössbauer spectra of anion exchanger washed in solution of $FeCl_3$

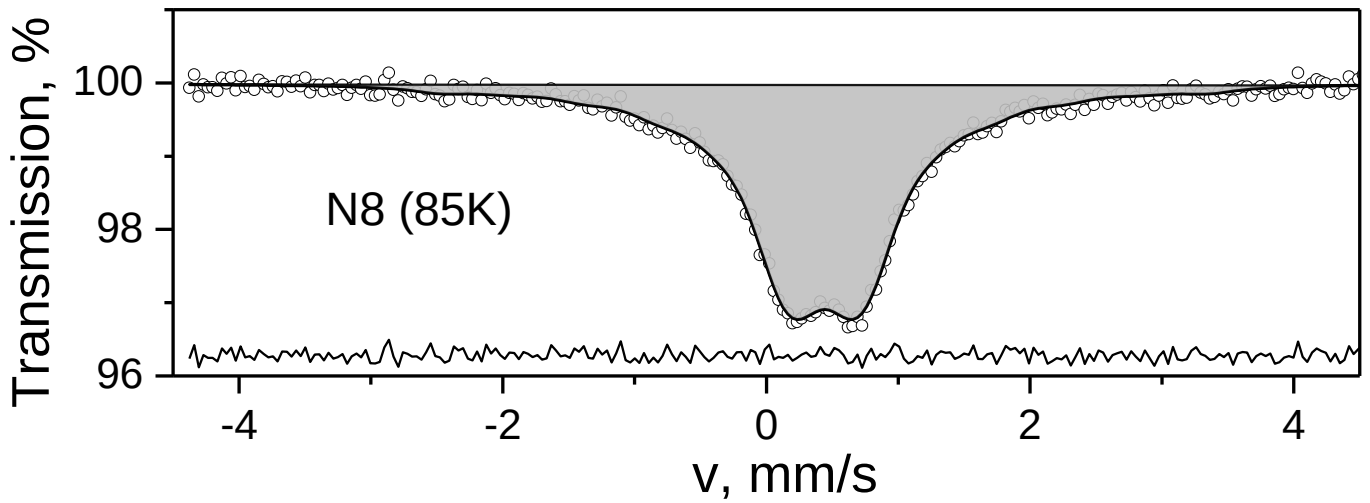


Fig. 5. Mössbauer spectra of anion exchanger Dowex 1X8 washed in solutions: *N8* – 0.1M FeCl3 + 6M HCl.

Table 3. Mössbauer parameters of samples of Dowex 1X8 washed in solutions of $FeCl_3$ (fig. 5).

Sample	Components	Is±0.01, mm/s	Qs±0.01, mm/s	Γ±0.01, mm/s	A±1, %	χ^2
N8 (85K)	[Δ]D1	0.32	2.50	0.30	100	0.875

Results and discussion: Mössbauer spectra of cation exchanger washed in solution of $Fe(NO_3)_3$

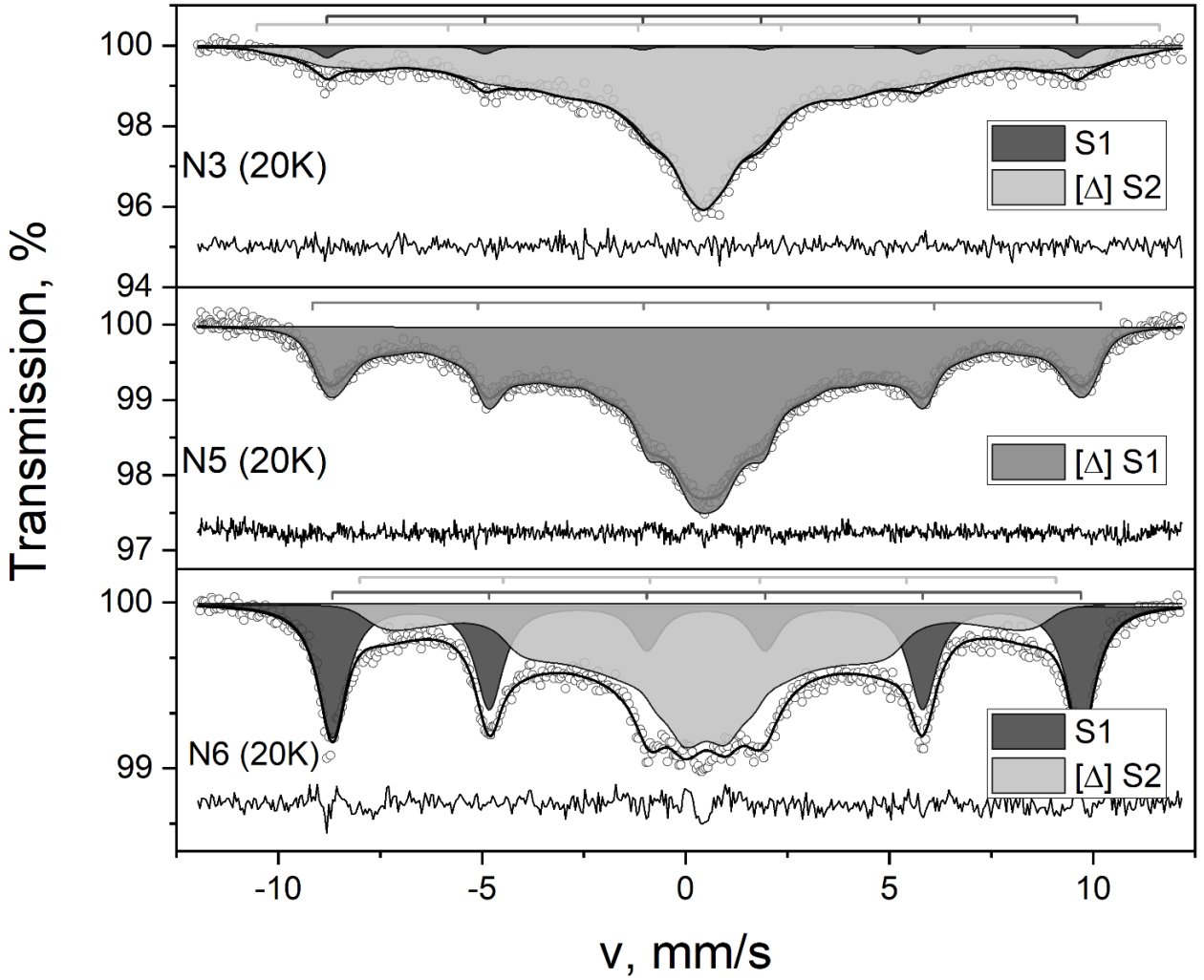


Fig. 6. Mössbauer spectra of cation exchanger Dowex 50WX8 washed in solutions: *N3* – 0.1M $Fe(NO_3)_3$; *N5* – 0.1M $Fe(NO_3)_3$ + 1M HNO_3; *N6* – 0.1M $Fe(NO_3)_3$ + 3M HNO_3

Table 4. Mössbauer parameters of samples of Dowex 50WX8 washed in solutions of $Fe(NO_3)_3$ (fig. 6).

Sample	Components	Is±0.01, mm/s	Qs±0.01, mm/s	H±1, kOe	Γ±0.01, mm/s	A±1, %	χ^2
N3 (20K)	S1	0.40	0.00	571	0.60	4.1	1.022
	[Δ]S2	0.56	0.00	600	0.60	95.9	
N5 (20K)	[Δ]S1	0.51	0.02	600	0.60	100	1.087
N6 (20K)	S1	0.51	0.02	574	0.69	28.1	0.957
	[Δ]S2	0.49	0.02	580	0.61	71.9	

Mössbauer spectroscopy: schematic diagram