Problems and solutions in the comprehensive diagnostics of some light metal hydrides

Prof. Lyudmila Levchenko

Nikolaev Institute of Inorganic Chemistry Siberian Branch RAS, Novosibirsk

- Creation of the “carbon -metal hydride” nanocomposition materials for effective hydrogen adsorption and development a such materials preparation”
- State contract № 02.513.11.3212, 18.05.2007

Aims of work:

Development of analytical methods and physical-chemical studies of some light metal hydrides and related nanocomposition materials. applied in H-storage

Some known light metal hydrides and their physical-chemical properties

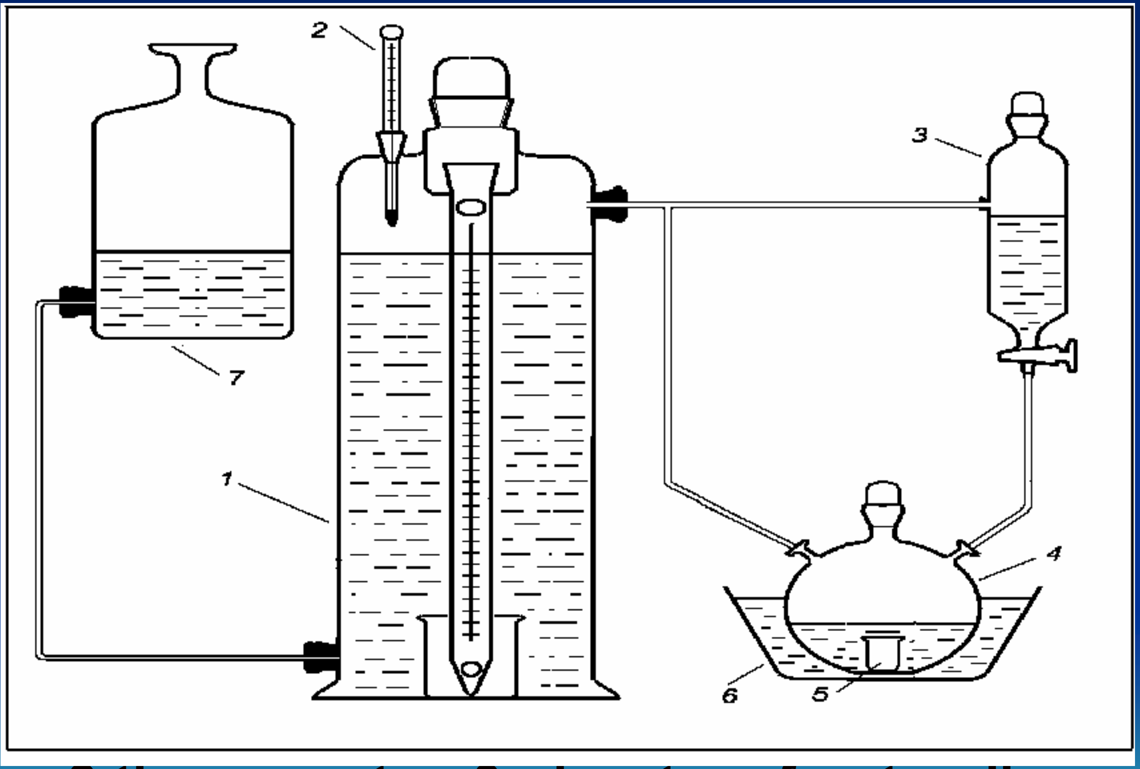
Compound	Density, g/cm^3	$\Delta H^o_{form.}$, kJ/mol	Hydrogen content, wt. %.	Melting point and decomposition temperature, ^oC
LiH	0.78	-90.7	12.68	M.p. 692, decomp. > 750
$LiBH_4$	0.681	-193.98	18.50	M.p. 283, decomp. > 283
AlH_3	1.45	-9.60	10.08	M.p.~150 , decom. > 283
MgH_2	1.42	-90.8	7.6	decomp. ~250-300
$LiAlH_4$	$0.917_{monocl.}$ $1.02_{tetrag.}$ $1.20_{rhomb.}$	-107.1	10.54	decomp. 75-230
$Mg[AlH_4]_2$	1.05	-234	9.34	118
$Ca[AlH_4]_2$		-184.3	7.89	пл. 185
TiH_2	3.78	-123.4	4.00	разл. 250-300
CaH_2	1.90	-186.2	4.75	пл. 815, разл> 850
NaH	1.38	-56.4	4.16	~ 800, разл> 850

Analyzed materials – chemicals from Novosibirsk Chemical Concentrates Plant, Aldrich and ABCR company

- LiH, Li[AlH4],
- Na[AlH$_4$], MgH$_2$

Gas-volumetric method of hydrogen determination, evoluted from hydrides through hydrolysis with water-dioxane mixture

T.N. Dymova, A.A. Vysheslavtsev, // Russ. J. Inorg. Chem. 1960, v.5, pp.2153-2156



1- gazometer, 2-thermometer; 3- dosator of water-dioxane solution; 4- reaction flask; 5- analyzed sample; 6- cooling bath; 7- level receiver

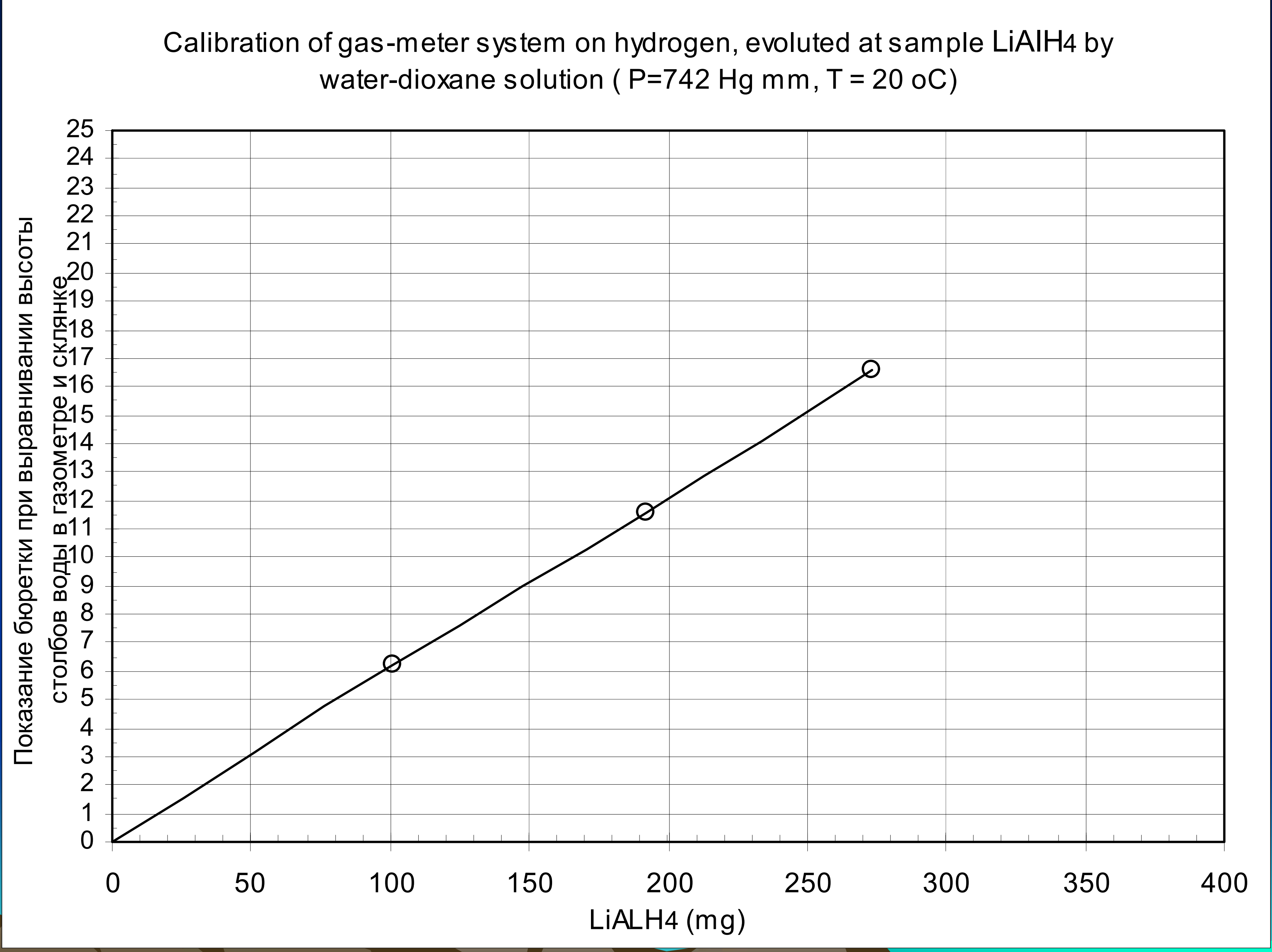
Method of H determination in $LiAlH_4$ and related nanocomposition materials

- 1) Registration of gas-meter and thermometer values.
- 2) Loading of water-dioxane mixture into dosator vessel.
- 3) Insertion of analyzed H-sample $LiAlH_4$ into flask.
- 4) Closing of gas-meter.
- 5) Installation of reaction flask into cooling bath.
- 6) Introduction of water-dioxane mixture up to stop of H_2 evolution.
- 8) Fixation of gas-burette value.
- 9) Normalization of gas-burette values to normal condition and calculation of $LiAlH_4$ amount, accordingly to calibration graph.
- 10) Calculation or graphical detemination of the evoluted hydrogen.

Calculation reaction

$$LiAlH_4 + 4H_2O = LiOH + Al(OH)_3 + 4H_2$$

Amount LiAlH4 (mg)	38	100	150	190	200	285	300	380	400
Water amount for hydrolysis (ml)	0,07	0,19	0,29	0,36	0,38	0,54	0,57	0,72	0,76


Calibration of gas-meter system on hydrogen, evoluted at sample LiAlH4 by water-dioxane solution (P=742 Hg mm, T = 20 oC)
Показание бюретки при выравнивании высоты столбов воды в газометре и склянке
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
0
50
100
150
200
250
300
350
400
LiALH4 (mg)

Meaning of calculation coefficients for "normal" conditions at various p, T

T, ^{O}C	P, mm Hg						
	732	**734**	**736**	**738**	**740**	**742**	**744**
18	0,9035	0,9059	0,9084	0,9109	0,9134	0,9158	0,9183
19	0,9004	0,9028	0,9053	0,9078	0,9102	0,9127	0,9151
20	0,8973	0,8997	0,9022	0,9046	0,9071	**0,9096**	0,9120
21	0,8942	0,8967	0,8991	0,9016	0,9040	0,9065	0,9089
22	0,8912	0,8936	0,8961	0,8985	0,9010	0,9034	0,9058
23	0,8882	0,8906	0,8930	0,8955	0,8979	0,9003	0,9028

Analysis of $LiAlH_4$ in THF (THF –tetrhydrofurane)

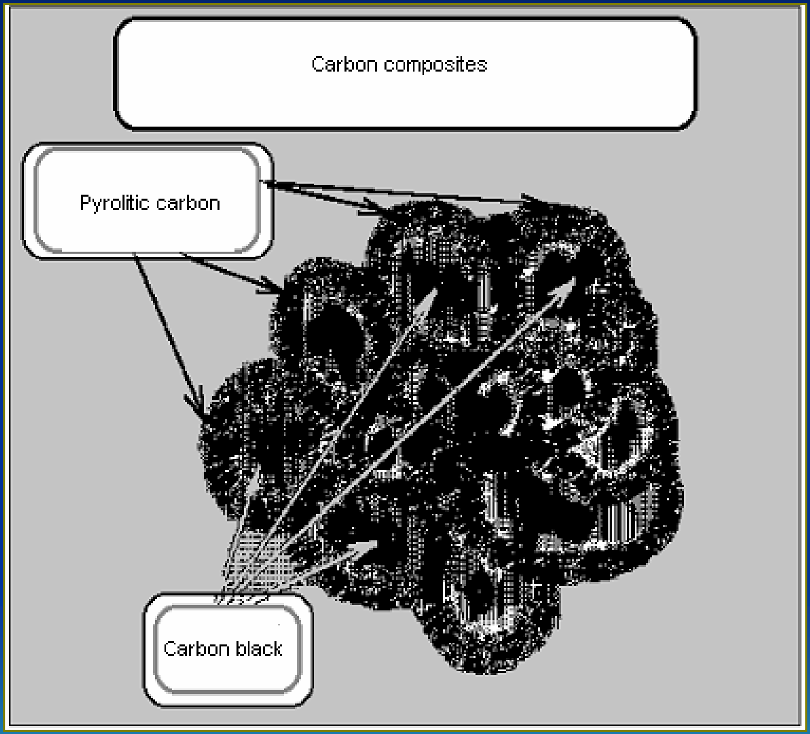
Solution weight (g)	**Calculated volume, through ρ (ml)**	Passport amount $LiAlH_4$ in solution sample (mg)	Gas-meter data at P=744 mm Hg T= 23 ^{O}C	Normalized gas-meter data (K = 0,90)	Found amount $LiAlH_4$ in solution sample (mg)	Found concentration $LiAlH_4$ in THF solution, (mol/l)
4.4436	4.68	178	13.0	11.7	202	1.14±0.01

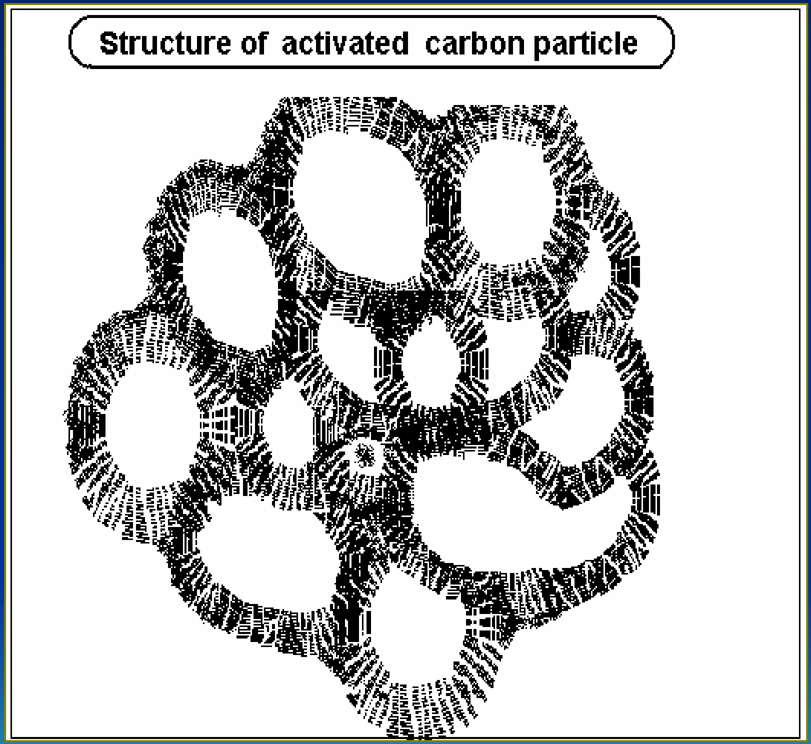
- Passport concentration – 1 M LiAlH4 - THF, at ρ=0,95.

Material balances at analyses of the matrix and microcontaminations of H-bering samples

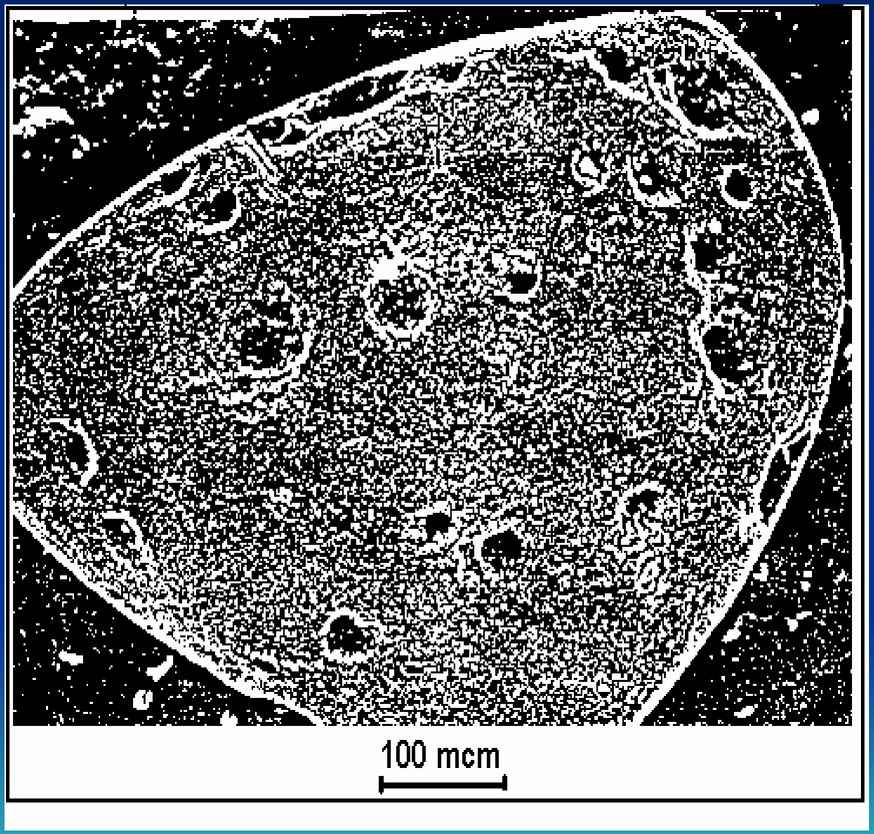
Component	Found in samples, wt. %; n = 3-5					
	$LiAlH_4$, Aldrich	$LiAlH_4$, ABCR	$NaAlH_4$, ABCR	MgH_2, ABCR	Mg, ABCR	Al, ABCR
Li	18.80±0.2 theor. 18.28	19.0±0.2	1.33±0.02 $_*10^{-4}$	1.73±0.42 $_*10^{-4}$	5.3±0.9 $_*10^{-5}$	N/A
Al	73.73±2.14 theor. 71.09	69.85±3.64 theor. 71.09	48.86±4.12 theor. 49.96	<2.0$_*10^{-3}$	$2{\cdot}10^{-2}$	99.773
Na	0.037 ±0.002	0.042 ±0.002	43.8±0.2 theor. 42.57	0.0077 ±0.0022	0.0019 ±0.0002	$6{\cdot}10^{-4}$
Mg	5.0$_*10^{-3}$	1.5$_*10^{-3}$	2.0$_*10^{-3}$	94.8±3.6 theor. 93.34	99.885	0.003
H	10.54±0.06 theor 10.62	10.57±0.01 theor 10.62	7.42±0.02 theor 7.46	7.40±0.03 theor 7.66	N/A	N/A
Contaminations (table 2)	0.0494	0.0454	0.019	0.0739	0.1148	0.157 (0.195)*
Matrix, wt. %	103.1±2.40	99.42±3.85	100.08±4.16	102.5±3.69	99.885 ±0.025	99.843±0.07
Total value, wt. %	103.1±2.41	99.47±3.85	100.1±4.16	102.6±3.7	100	100

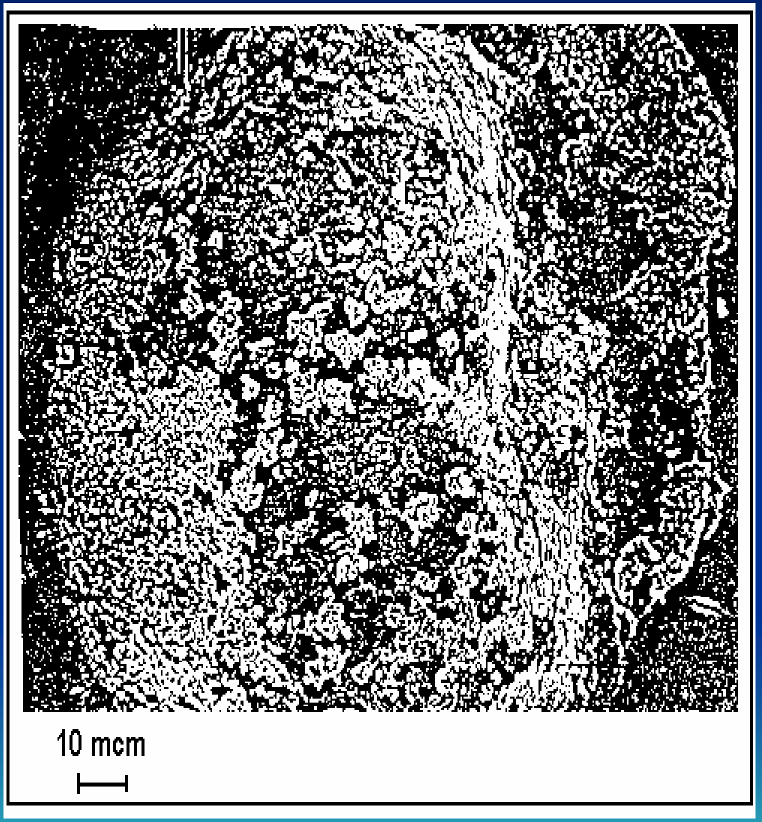
Carbon composite matrix preparation by depositing of pyrolytic carbon on the surface of carbon black with the subsequent steam activation



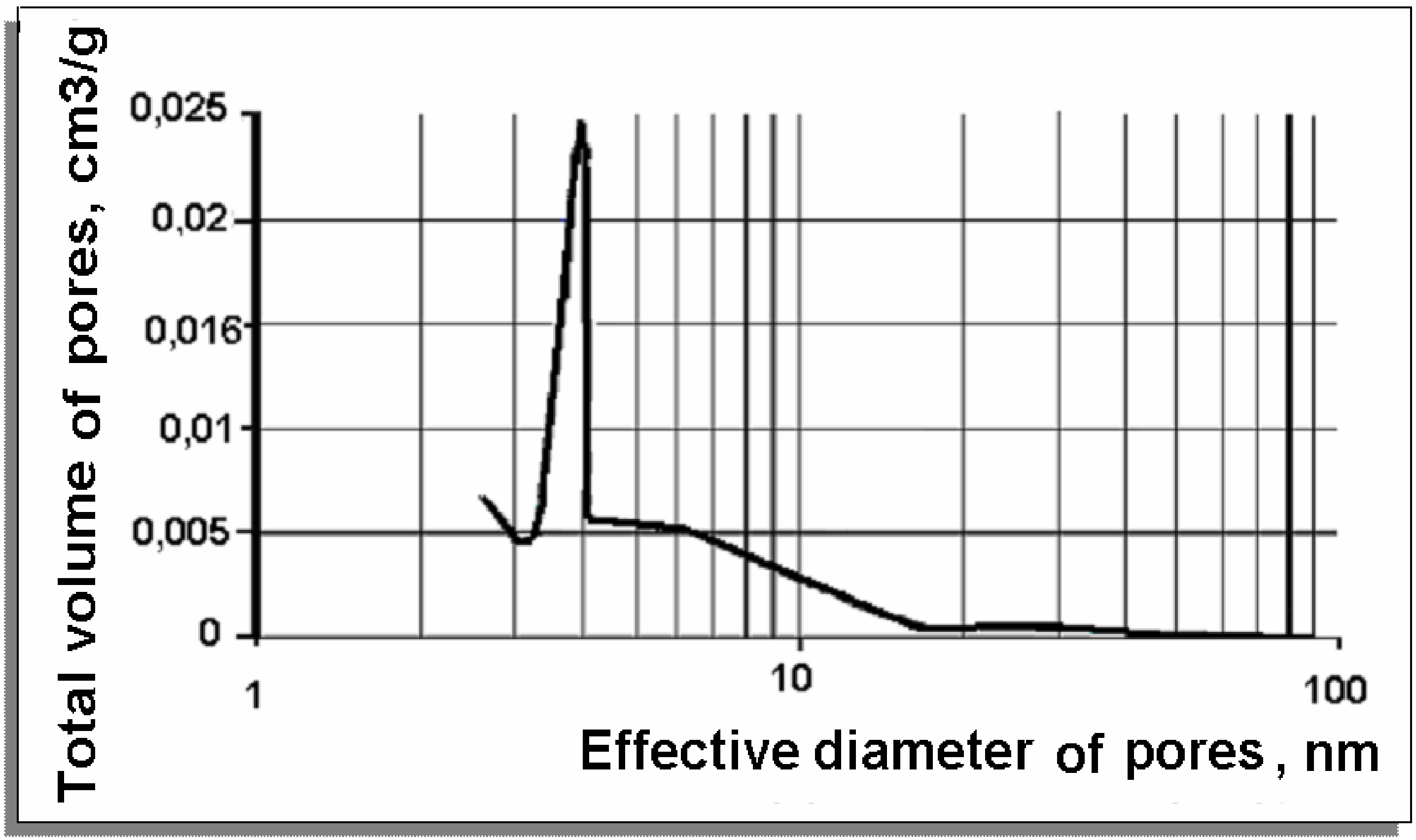


EMS microphotographs of starting carbon matrix and NCCM sorbent particles

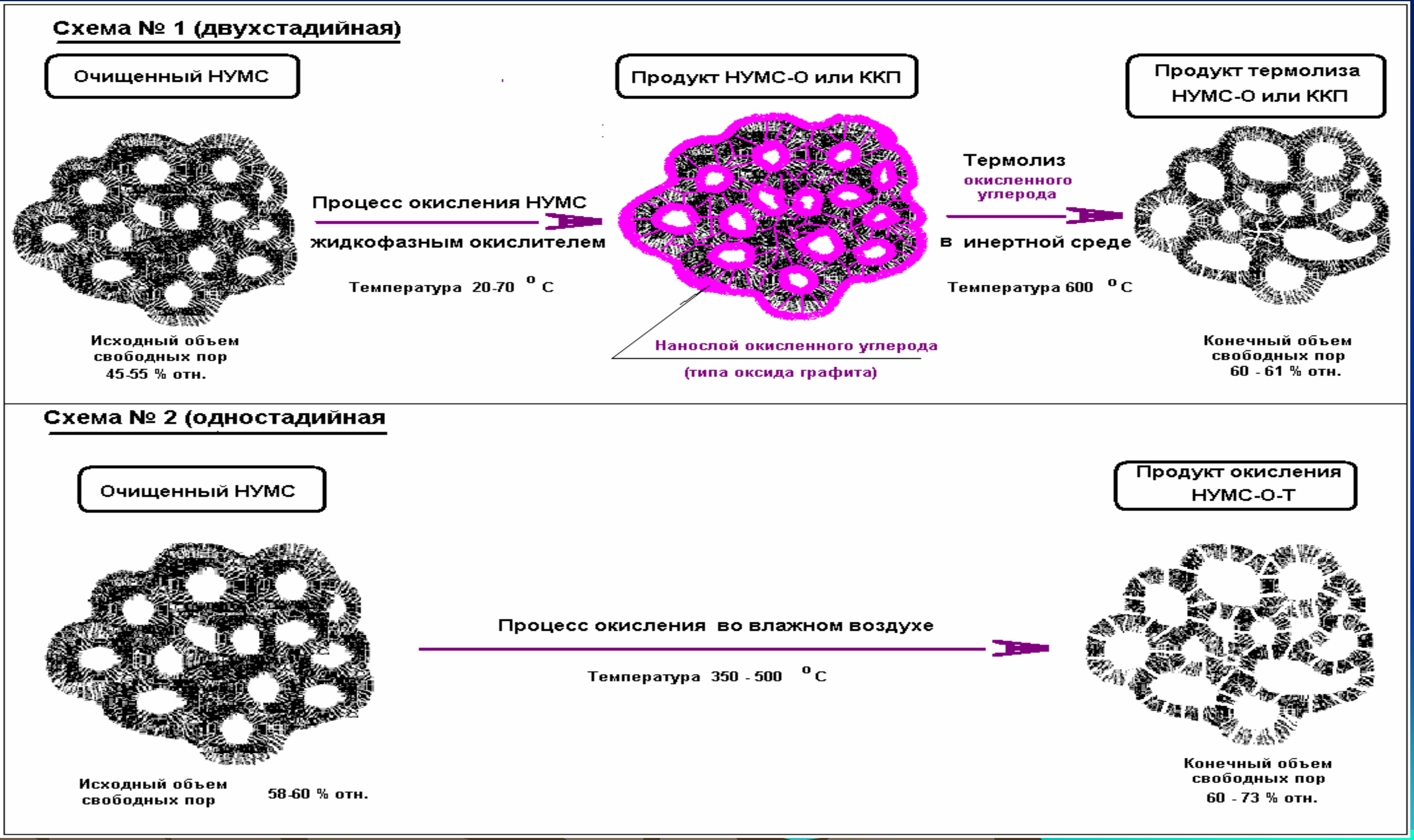




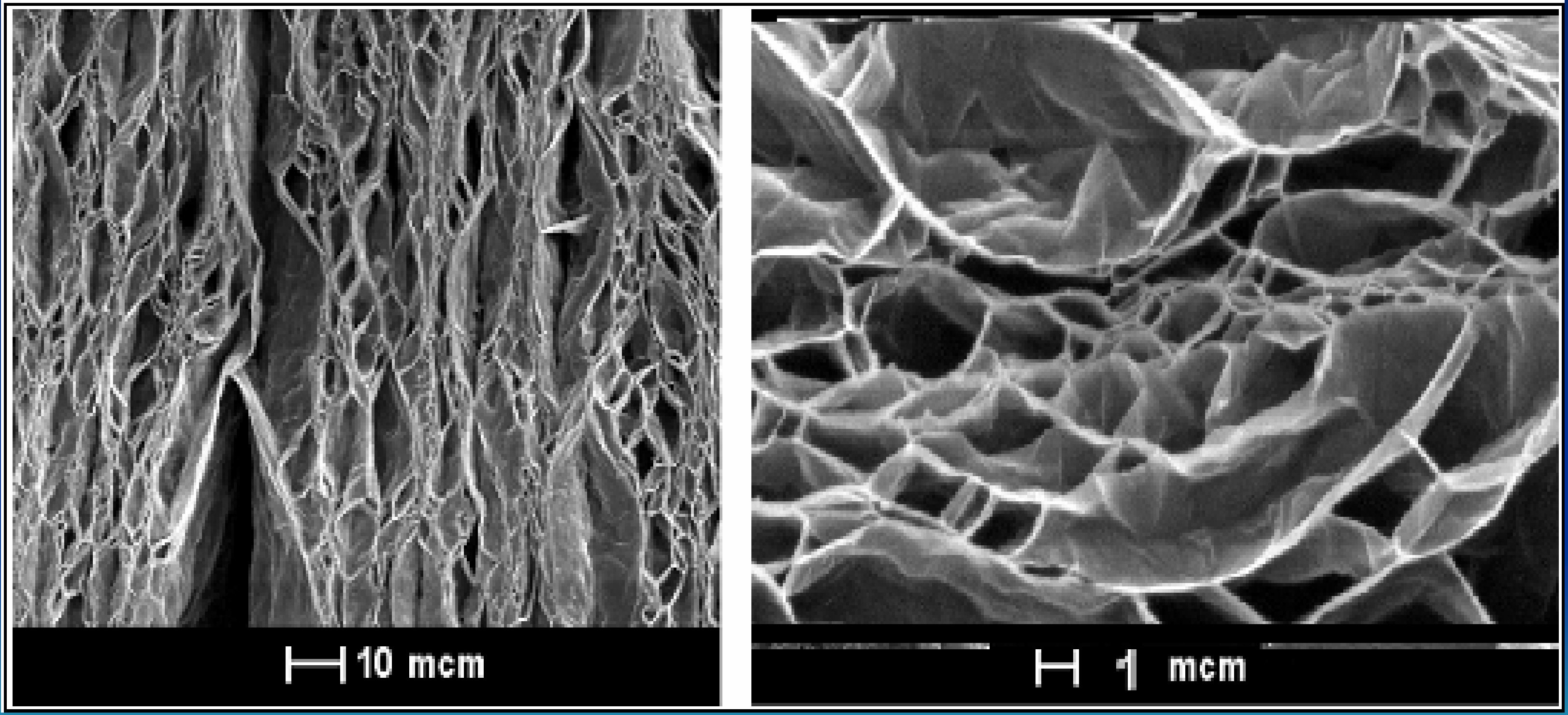
The dependence of total volume on effective pore's diameter



Two ways for porous C-matrix preparation



High purity thermal expanded graphite TEG-400 (FVP – 95%)



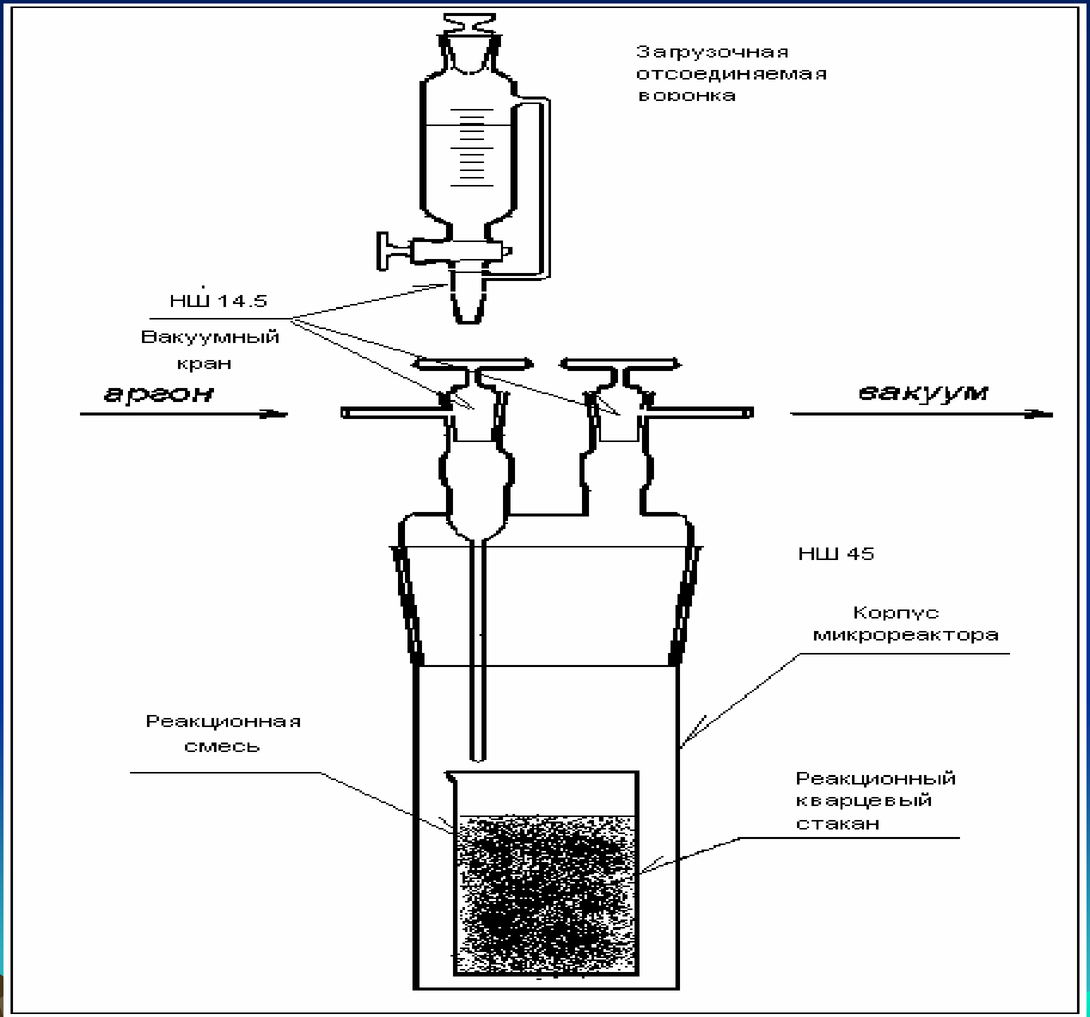
Content of microlements in the starting and obtained C-matrices

Element and analytical spectral line, nm	Found, $C \pm (t_{st}S_r C)/\sqrt{N}$ (N = 8-20), ppm (10^{-4} $\%_{мас.}$) t_{st} – table meaning for P=0.95 and ν = N-1				
	Natural graphite	PURIFIED Graphite	TS - Starting technosorb	Purified TS	NUMS-O LP-method
Al I 308.2151	0.62 $\%_{мас.}$	270± 24	54.7± 8.5	12.1±2.1	15.6±3.1
Ba I 223.061	200 ppm	...	1.33 ± 0.12	0.42±0.063	0.42±0.043
Ca II 318.1275	1.62 $\%_{мас.}$	910±10	369± 53	6.7±3.9	6.42±0.61
Cd I 346.62	45 ppm	3.18± 0.24	0.12± 0.045	1.6±0.13	1.5±0.12
Cr II 267.717	230 ppm	1.50±0.02	11.5± 1.5	4.6±0.16	5.03±0.37
Cu I 327.3954	240 ppm	21±0.3	1.48± 0.15	0.92±0.11	0.47±0.032
Fe I 248.8143	1.39 $\%_{мас.}$	730 ± 59	124±14	1.5± 2.6	4.2±3.0
Mg I 285.2126	0.82 $\%_{мас.}$	700±169	10.9±0.86	4.04± 0.53	2.19±0.085
Mn I 324.8512	600 ppm	121± 5	3.62± 0.42	2.81±0.47	1.26±0.18
Mo I 313.2594	30 ppm	1.40±0.03	2.88±0.56	2.87±0.52	2.79±0.54
Ni I 313.4106	74 ppm	5.1± 0.9	13.8±1.4	6.3± 1.8	6.77±0.35
Si I 288.1579	1.23 $\%_{мас.}$	937±27	23.1± 2.4	11.6±1.1	7.91±0.57
Sn I 277.982	0.12 $\%_{мас.}$	616± 13	9.97± 0.79	4.95±1.3	4.64±0.36
Total contamines, ppm	5.49 wt. %	4360 ± 311	713 ± 97	72 ± 17	65 ± 10

Ar-glove box for preparation of the starting mixes to a syntheses of the “carbon-MH” nanocomposites

- Metal hydrides and nanocomposites “C-MH” are unstable at their contact in Lab Air. All operations were conducted in dry Ar-glove boxes (dryer - P_2O_5).
- All Ar-boxes were specialized for exact operations.
- First box – re-packing of H-materials and chemicals (LiH, LiAlH4 and 1 M solution $LiAlH_4$ in THF) to a small vessels.
- Second Ar-box – processing of “C-MH“ nanocomposites by means of leaching with usage of special microreactor.
- Third Ar-box – mechanosynthesis of “C-MH”

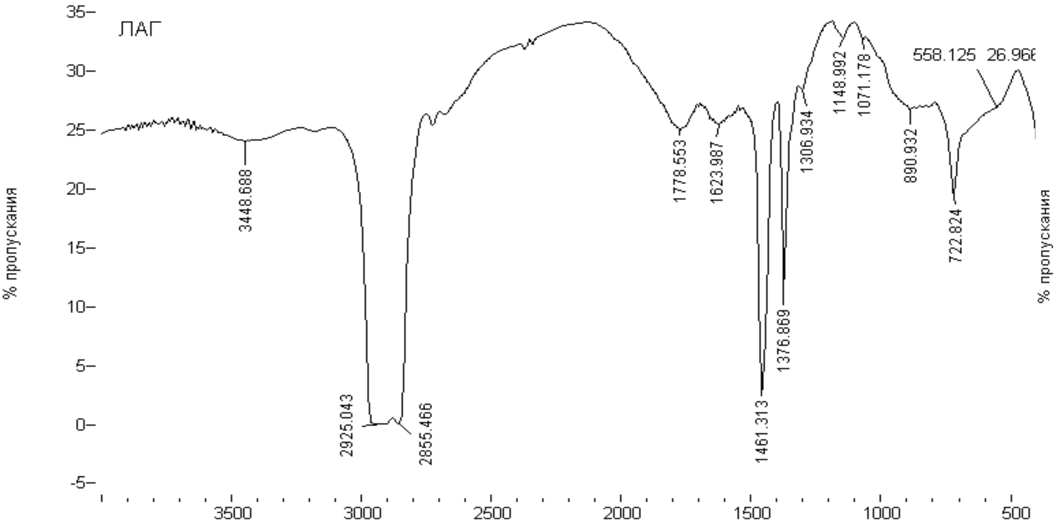
Quartz microreactor for “C-MH“ nanocomposites syntheses

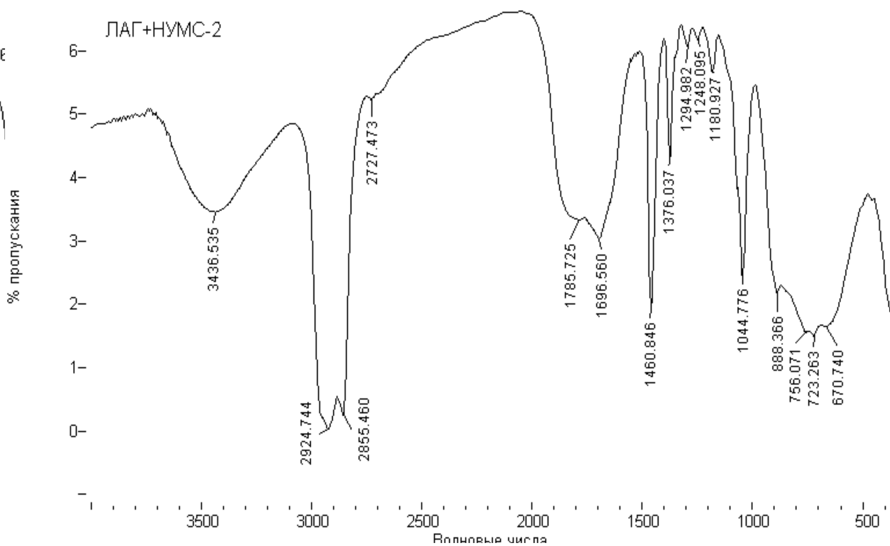


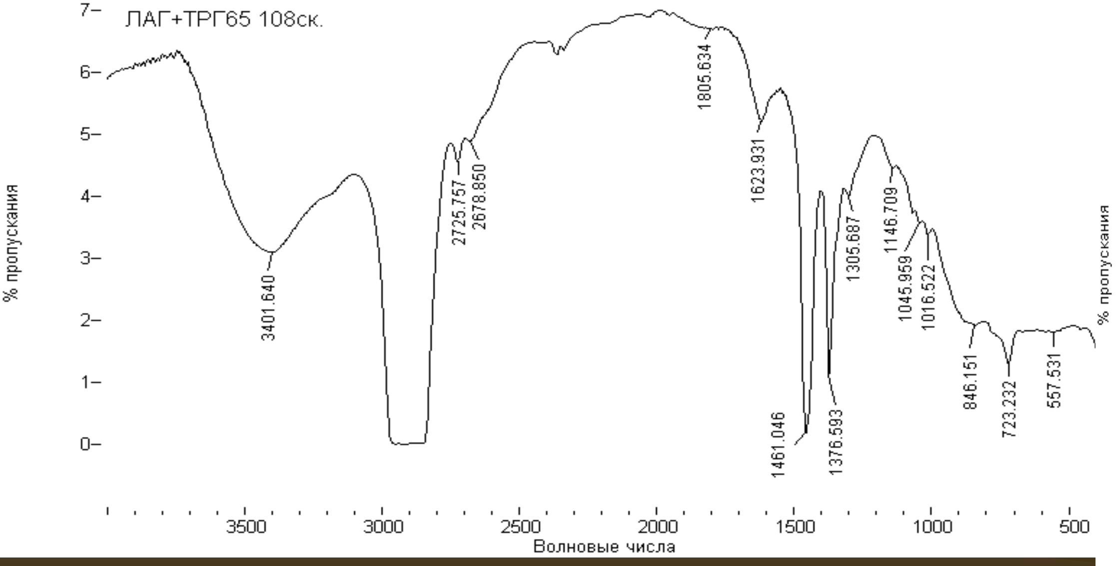
"C-MH" nanocomposites analyses on H-content

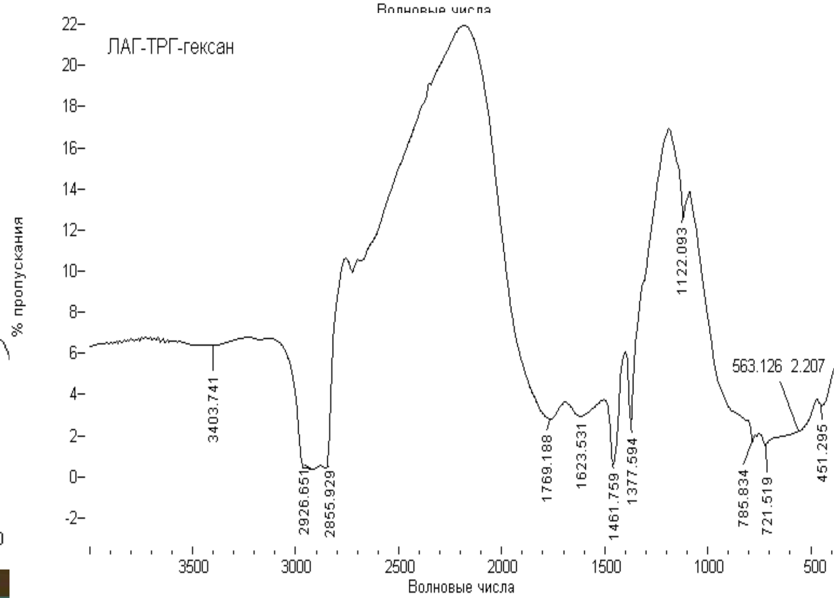
Sample type	Sample portion. mg	Gas-meter Values, cm^3	Gas-meter Values Norma-lized, Cm^3	Amount of $LiAlH_4$ in a sample (mg)	Per cent of active $LiAlH_4$ In a sample, rel. %	H_2 volume for a such $LiAlH_4$ amount (cm^3)
Composite after evaporation of THF from leaching solution $LiAlH_4$ in THF	162	0.7 P=738 мм Hg T=23.5^{O}C	0.63 (K=0.894)	11	6.8	26
TEG-LAH-THF	246	1.0 P=736 мм Hg T=24^{O}C	0.9 (K=0.89)	15	6.1	35
NUMS-LAH-THF	365	1.3 P=738 мм Hg T=22 ^{O}C	1.15 (K=0.9)	18	4.9	42.5
TEG-LAH-DBE	330	3.5 P=738 мм Hg T=23 ^{O}C	1.2 (K=0.896)	55	16.5	130
NUMS-LAH-DBE	309	8.5 P=738 мм Hg T=22 ^{O}C	7.65 (K=0.9)	132	42.6	310
TEG-LAH-Hexane	290	15.5 P=738 мм Hg T=22 ^{O}C	14.0 (K=0.9)	240	82.5	567
NUMS-LAH-hexane	255	13.3 P=738 мм Hg T=22 ^{O}C	12.0 (K=0.9)	207	81.0	490

FTIR-spectra of Li alanates

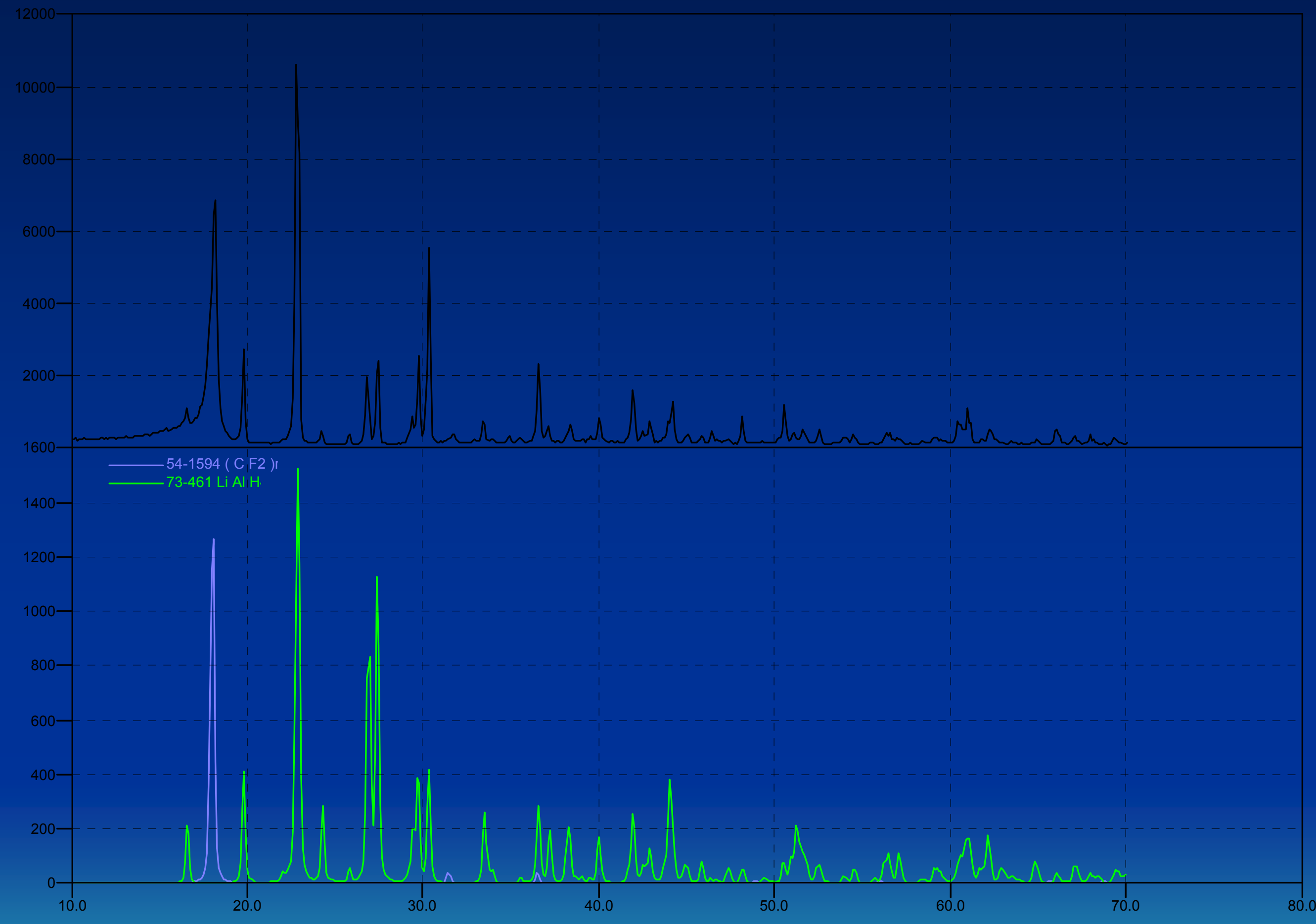








Difractogram for $LiAlH_4$



Conclusions:

- Aldrich and ABCR samples are available for R&D in the field of H-storage materials,
- No toxic elements in Aldrich and ABCR MH-chemicals,
- No reference samples of MH-hydrides in Russia and in the World,
- No certified methods for analyses of MH-samples in Russia (except LiH – NCCP production) in Russia and in the World
- Lab methods for analyses of MH-samples (main matrix components) needs of improvement and certification,
- All Russian Labs needs of Russian MH-chemicals for further development
- World Labs also needs of reference samples and analytical methods