Scientific Papers of the University of Pardubice, Series A; Faculty of Chemical Technology **25** (2019) 127–139.



# Evaluation of lithium salts as propellant components

Milan Jančík<sup>1</sup>, Zdeněk Jalový<sup>1</sup>\*, Robert Matyáš<sup>1</sup>, Jan Zigmund<sup>2</sup>, Radovan Skácel<sup>2</sup>, and Pavla Honcová<sup>3</sup>

<sup>1</sup> Institute of Energetic Materials, The University of Pardubice, CZ–532 10 Pardubice, Czech Republic <sup>2</sup> Explosia a.s., CZ–530 50 Pardubice, Czech Republic <sup>3</sup> Department of Inorganic Technology, The University of Pardubice, CZ–532 10 Pardubice, Czech Republic

Received: June 14, 2019; Accepted: July 25, 2019

Lithium nitrotriazolone dihydrate (LiNTO), lithium ethylenedinitramine hemihydrate (LiEDNA), dilithium ethylenedinitramine dihydrate (Li2EDNA), lithium 5-aminotetrazolate (LiATZ), lithium bis(2,4,6-trinitrophenyl)amine hydrate (LiHexyl), lithium 2,4,6-trinitrophenolate hydrate (LiTNF), and lithium 2,4,6-trinitroresorcinate dihydrate (LiTNR) have been prepared and evaluated with respect to their potential use as a component in the so-called green propellants. Densities and DTA decomposition temperatures were determined. The heat of formation of lithium 5-aminotetratolate was measured using an isoperibolic twin calorimeter. Sensitivities to impact and friction were defined to evaluate handling safety.

**Keywords**: Lithium salts; Preparation; Sensitivity; DTA; Density; Heat of formation

#### Introduction

Ballistic modifiers are an important component of rocket propellants. In double-based propellants, compounds containing heavy metals, such as the oxides, stearates and resorcinates of lead and copper are used as ballistic modifiers. In the composite propellants, ferrous oxide, cuprous oxide, ferrocene or lithium fluoride are frequently used. These compounds support the effect of *plateau* or *meza* burning, when the burning rate does not depend on the pressure in the combustion chamber [1–3].

<sup>\*</sup> Corresponding author, ⊠ zdenek.jalovy@upce.cz

Various lithium compounds are suitable for gas-generating propellants [4] in safety systems of transport vehicles, where they may replace strontium compounds. Such *green propellants* contain ammonium perchlorate as an oxidizer and by their reaction with strontium, sodium or lithium they form rather non-toxic chloride compounds. The advantage of lithium chloride over strontium chloride is the low molecular weight of lithium which enhances the *force* of the propellant about 15 % (see [5]).

The lithium salts are also of interest as non-toxic coloring agents in modern pyrotechnics yielding a red pyrotechnic flame [6–8]. Among promising compounds in this area, one has those with a high nitrogen content and a low carbon content, such as the tetrazole salts [9,10].

In this work, several lithium salts have been prepared and studied in order to find suitable material that can be used in propellant safety systems containing ammonium perchlorate or potassium perchlorate. The lithium present in compounds as a cation bonds the chlorine originating from the perchlorate. The rest of the molecule should contain high nitrogen content and/or an energetic group as a source of oxygen and energy.

#### Materials and methods

The thermal analysis was studied using a DTA 550Ex differential thermal analyzer (OZM Research, Hrochův Týnec, Czech Republic). The samples were tested in open glass micro-test tubes in contact with the air with a heating rate of 5 °C min<sup>-1</sup>. The weight of samples was 10 mg. (An amount of 50 mg of lithium picrate led to an explosion with damage to the thermocouple!)

Thermo-gravimetric analyses were made using TG 209 F3 Tarsus (Netzsch, Selb, Germany). The weighted portion of samples was 2 mg, heating rate of 5 °C min<sup>-1</sup>, and a nitrogen atmosphere with 30 mL min<sup>-1</sup> was used. The melting points were measured on a Kofler bench and are uncorrected. If no melting occurred before reaching 360 °C, it is stated as >360 °C.

The infrared spectra were collected using a Nicolet iS50 FT-IR spectrometer (Thermo Fisher Scientific, Medison, WI, USA) with an ATR single reflection diamond accessory GladiATR (PIKE Technologies, Madison, WI, USA) and a zinc selenide ten reflection ATR accessory GladiATR (PIKE Technologies). Measurement parameters were: the spectral region 4000–400 cm<sup>-1</sup>, resolution 4 cm<sup>-1</sup> and number of scans 64.

Densities were measured using an Accu Pyc II 1340 helium pycnometer (MJ Micromeritics, Norcross, GA, USA) at 25 °C. The weight of the samples was from 200 mg to 500 mg weighed to one decimal place.

Elemental analysis was performed on the automatic device "Flash 2000 CHNS Analyzer" (Thermo Fisher Scientific, Waltham, MA, USA). Lithium content was determined using an Avanta AA 906 atomic absorption spectrometer (GBC Scientific Equipment, Braeside, Australia).

Enthalpy measurement was accomplished using an isoperibolic twin calorimeter at 25 °C [11], when the exothermic reaction of hydrochloric acid with sodium hydroxide was used for calibration.

A BFH-12 Kast fall hammer (OZM Research) was used for determining the impact sensitivity using a 2 kg hammer for PETN and RDX, a 5 kg hammer for Li<sub>2</sub>TNR and LiTNF and a 10 kg hammer for the other samples. Cylinders BFH-SR and guide rings BFH-SC (OZM Research) were used for measuring. The modified Neyer's sensitivity D-optimal test method [12] was used both for measuring and for evaluation. Thirty tests were carried out for each sample.

Sensitivity to friction was determined using an FSA-12 BAM type friction apparatus (OZM Research) in combination with porcelain plates BFST-Pt and porcelain pegs BFST-Pn (OZM Research) used for measurements. The modified Neyer's sensitivity D-optimal test method [12] was used both for measuring and for evaluation. Again, thirty tests were carried out for each sample.

Pentaerythritol tetranitrate (PETN) and hexogen (RDX) were used as standard explosives for comparison of sensitivities of lithium salts. Pentaerythritol tetranitrate under the trademark "PETN D" was obtained as a commercial product of Explosia Company; RDX being used with particle sizes  $100-300~\mu m$ .

The hygroscopicity of lithium salts was determined at 70% and 90% humidity, both at 30 °C [13]. For comparison, the hygroscopicity of sodium, potassium, and ammonium nitrates (common oxidizers used in explosives and pyrotechnics) was determined as well. Results are represented as the weight increase compared with the weight of the original sample, expressed in %.

### Preparation of lithium salts

Caution (!): The reported compounds are explosive and potentially sensitive to mechanical and thermal stimuli, such as friction, impact, heat, and electric spark. Safety equipment, such as goggles or a face-shield, gloves and ear protection are strongly recommended.

Lithium nitrotriazolone dihydrate (LiNTO) [14]

Nitrotriazolone (5.0 g, 38 mmol) was suspended in water (25 mL), the resulting mixture warmed to 50 °C and lithium hydroxide (1.0 g, 42 mmol) was added. Water was evaporated to dryness and the raw material recrystallized from ethanol to give 3.98 g (60.2 %) of a yellow solid. M.p. >360 °C. DTA: endotherm 102 °C

(onset), *exotherm* 282 °C (start), 289 °C (onset), 289 °C (maximum). Elemental analysis (C<sub>2</sub>H<sub>5</sub>LiN<sub>4</sub>O<sub>5</sub>): *Calc.* C 13.96, H 2.93, Li 4.03, N 32.57. *Found* C 13.93, H 2.83, Li 4.03 N 32.19. FTIR (cm<sup>-1</sup>): 3528, 3492, 3373, 3300, 3020, 2966, 2853, 2783, 1672, 1627, 1556, 1511, 1439, 1375, 1315, 1277, 1124, 1058, 1023, 856, 792, 776, 764, 736, 672, 606, 541.

### Lithium ethylenedinitramine hemihydrate (LiEDNA)

Ethylenedinitramine (3.0 g, 20 mmol) was suspended in water (15 mL) and lithium hydroxide (0.48 g, 20 mmol) added. Water was evaporated to give 2.6 g of a white solid (78.8 %). M.p. 176 °C. Elemental analysis (C<sub>4</sub>H<sub>12</sub>Li<sub>2</sub>N<sub>8</sub>O<sub>9</sub>): *Calc.* C 14.56 H 3.66 Li 4.21 N 33.95. *Found* C 14.62 H 3.86 Li 3.47 N 34.03. DTA: *endotherm* 90 °C (onset), *exotherm* 176 °C (start), 181 °C (onset), 182 °C (maximum). FTIR (cm<sup>-1</sup>): 3213, 3110, 3067, 2947, 1593, 1463, 1442, 1403, 1346, 1294, 1281, 1244, 1189, 1117, 1096, 994, 831, 788, 774, 750, 688, 598, 513, 468.

#### Dilithium ethylenedinitramine dihydrate (Li<sub>2</sub>EDNA)

Ethylenedinitramine (3.0 g, 20 mmol) was suspended in water (15 mL) and lithium hydroxide (0.96 g, 40 mmol) added. To the resulting solution, isopropylalcohol (35 mL) was added and the solid precipitated filtered and washed with isopropylalcohol to give 2.35 g of a white solid (59.3 %). M.p. 293 °C (dec., ref. [15] 274 °C). DTA: *endotherm* 93 °C (onset), *exotherm* 264 °C (start), 278 °C (onset), 279 °C (maximum) Elemental analysis (C<sub>2</sub>H<sub>8</sub>Li<sub>2</sub>N<sub>4</sub>O<sub>6</sub>): *Calc.* C 12.13 H 4.07 Li 7.01 N 28.30. *Found* C 12.27 H 4.05 Li 6.98, N 28.62. FTIR (cm<sup>-1</sup>): 3107, 3050, 2947, 1594, 1463, 1438, 1277, 1189, 1095, 994, 826, 789, 748, 689, 606, 509.

### Lithium 5-aminotetrazolate (LiATZ)

5-Aminotetrazole (127.5 g, 1.50 mol) was dissolved in methanol (1 L) at a temperature of 50 °C and lithium hydroxide (36.0 g, 1.50 mol) in methanol (1 L) added at the same temperature. The mixture was stirred for 45 min. The volume of the reaction mixture was reduced to 100 mL by evaporation of methanol using a rotary vacuum evaporator. The resulting solid was filtered and washed with methanol and finally with acetone to give 99.1 g of a white solid (72.7 %). M.p. >360 °C. DTA: exotherm 352 °C (start), 361 °C (onset), 469 °C (maximum). TG: 388 °C (weight loss, start), 395 °C (weight loss, onset). Elemental analysis

(CH<sub>2</sub>LiN<sub>5</sub>): *Calc*. C 13.20, H 2.22, Li 7.63, N 76.69. *Found* 13.26, H 2.14, Li 7.18, N 76.43. M.p. >360 °C. FTIR (cm<sup>-1</sup>): 3356, 3217, 1617, 1519, 1484, 1467, 1243, 1150, 1128, 1093, 1029, 820, 755, 718, 545, 470.

### Lithium bis(2,4,6-trinitrophenyl)amine hydrate (LiHexyl)

Bis(2,4,6-trinitrophenyl)amine (1.5 g 3.42 mmol) was suspended in acetone (25 mL) and lithium hydroxide hydrate (145 mg, 3.46 mmol) added. The solvent was evaporated to give 1.46 g of a red solid (91.5 %). M.p. 225–226 °C. DTA: *exotherm* 298 °C (start), 317 °C (onset), 320 °C (maximum). Elemental analysis (C<sub>12</sub>H<sub>6</sub>LiN<sub>7</sub>O<sub>13</sub>): *Calc.* C 31.12, H 1.31, Li 1.50, N 21.17. *Found* C 31.22, H 1.25, Li 1.19, N 21.30. FTIR (cm<sup>-1</sup>): 3625, 3603, 3557, 3095, 1618, 1592, 1574, 1533, 1522, 1484, 1414, 1376, 1311, 1276, 1248, 1190, 1163, 1085, 944, 915, 878, 828,815, 765, 733, 720, 703, 675, 648, 538, 483.

### Lithium 2,4,6-trinitrophenolate hydrate (LiTNF)

Picric acid (4.58 g, 20 mmol) was suspended in water (20 mL) at room temperature, lithium carbonate (0.746 g, 10.1 mmol) slowly added, and the mixture stirred for ten minutes at room temperature. Then the reaction mixture was heated to 60 °C and stirred for 15 min. The unreacted lithium carbonate was filtered off and water allowed to evaporate from the filtrate until crystallization of the solid product occurred. Then the mixture was cooled to 0 °C and the precipitated product filtered, and then washed with a small amount of cold water to give 2.90 g of a yellow solid (61.7 %). M.p. 308–313 °C (ref. [16] 301.2 °C). DTA: *endotherm* 314 °C (onset), *exotherm* 325 °C (maximum). Elemental analysis (C<sub>6</sub>H<sub>6</sub>LiN<sub>3</sub>O<sub>9</sub>): *Calc*. C 28.48, H 1.59, Li 2.74, N 16.16. *Found* C 28.64, H 1.46, Li 2.54, N 15.75. FTIR (cm<sup>-1</sup>): 3604, 3550, 3094, 1611, 1568, 1547, 1488, 1418, 1367, 1336, 1314, 1252, 1160, 1083, 942, 914, 839, 832, 792, 742, 707, 551, 521.

## Lithium 2,4,6-trinitroresorcinate dihydrate (Li<sub>2</sub>TNR)

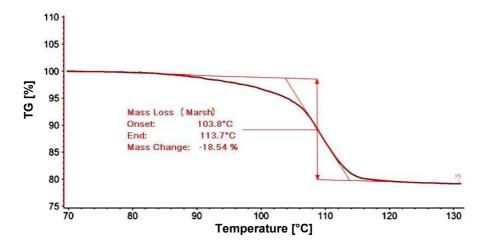
Styphnic acid (7.53, 30.7 mmol) was dissolved in ethanol (70 mL) at 45 °C, lithium carbonate (2.59 g, 35.0 mmol) added, and the mixture was stirred at the same temperature for 15 min. The unreacted lithium carbonate was filtered off and the filtrate concentrated by evaporation of ethanol using a rotary vacuum evaporator until the solid product started to form. The resulting solution was cooled to 0 °C and the precipitated product filtered, washed with a small amount of cold ethanol to give 0.56 g (6.3 %) of a yellow solid.

M.p. >360 °C. DTA: exotherm 300 °C (start), 317 °C (onset), 317 °C (maximum). Elemental analysis ( $C_6H_5LiN_3O_{10}$ ): Calc. C 24.60, H 1.72, Li 4.74, N 14.34. Found C 24.49, H 1.91, Li 4.49, N 13.94. DTA: exotherm 305.6 (start), 317.5 (onset), 318.1 (maximum). FTIR (cm<sup>-1</sup>): 3535, 3445, 3074, 3030, 1632, 1575, 1530, 1496, 1427, 1320, 1310, 1227, 1153, 1109, 982, 955, 915, 839, 799, 776, 766, 748, 703, 559, 490, 458.

#### **Results and discussion**

Lithium salts were prepared by the reaction of the starting material and lithium hydroxide or lithium carbonate. In order to evaluate the hydrates, elemental analysis, FTIR and TGA methods were used to estimate crystal hydrate water. Using FTIR, the bands generally in the region 3670–3400 cm<sup>-1</sup> indicate the presence of free or hydrogen bonded water [17]. The particular bands for the compounds prepared are as follows: LiNTO (3527 cm<sup>-1</sup> and 3486 cm<sup>-1</sup>), LiHexyl (3625 cm<sup>-1</sup> and 3603 cm<sup>-1</sup>), LiTNF (3604 cm<sup>-1</sup> and 3550 cm<sup>-1</sup>) and Li<sub>2</sub>TNR (3535 cm<sup>-1</sup> and 3445 cm<sup>-1</sup>). When LiTNF was heat-exposed to 180 °C, the bands at 3604 cm<sup>-1</sup> and 3550 cm<sup>-1</sup> disappeared in the FTIR spectrum.

The TG thermogram for lithium nitrotriazolone is illustrated in Fig. 1, with a mass loss of 18.6 %, against a theoretical value for the dihydrate of 20.9 %. Using the same method, LiTNF loses 6.4 % wt. by heating between 80 °C and 180 °C. This weight loss corresponds to the liberation of one molecule of crystal water (theoretically 7.1% weight loss). In the case of lithium styphnate, the TG analysis confirmed that Li<sub>2</sub>TNR loses 14.5 % wt. by heating between 80 °C and 220 °C which corresponds to the release of two molecules of crystal water (theoretically 14.0 % weight loss).



**Fig. 1** TG thermogram of lithium nitrotriazolone in the region from 70 °C to 130 °C indicating the loss of the hydrate water

The densities of the lithium compounds vary from 1.7 g cm<sup>-3</sup> to 1.9 g cm<sup>-3</sup> and decomposition temperatures determined by DTA are usually over 200 °C as shown in Table 1.

Table 1	Start of decomposition by DTA and densities of the prepared lithium salts plus
	comparisons with PETN and RDX

Compound	Start of decomposition, DTA [°C]	Density [g cm <sup>-3</sup> ]		
LiNTO	282	1.91		
LiEDNA	176	1.69		
Li <sub>2</sub> EDNA	264	1.74		
LiATZ	352	1.71		
LiHexyl	298	1.77		
LiTNF	314 <sup>a</sup>	1.75		
Li <sub>2</sub> TNR	300	1.90		
PETN	140 <sup>a</sup>	1.78 <sup>b</sup>		
RDX	202 <sup>a</sup>	1.82 <sup>b</sup>		

<sup>&</sup>lt;sup>a</sup> onset of *endotherm* that pass continuously to *exotherm*, <sup>b</sup> values from [15]

For calculating the energetic properties of propellant- or pyrotechnic formulations, the heat of formation is one of the crucial parameters. One of the frequently used methods is based on calculation of the formation enthalpy from a measured heat of combustion. In our case, using a high pressure oxygen calorimeter, some unburnt species remained left after burning. If the sample is combusted with a smokeless propellant, the burning is completed; however, lithium present in the compounds forms the lithium oxide after burning. Lithium oxide may react with water vapor present in the calorimeter, as well as with water as a combustion product to form lithium hydroxide. Unfortunately, the ratio of lithium oxide and hydroxide is impossible to estimate and the calculated values of enthalpy of formation are different if calculated for lithium oxide or for lithium hydroxide. That is why another method was chosen for heat of formation based on determining the heat of reaction for the reaction of 5-aminoterazole and lithium hydroxide in water (Fig. 2).

$$NH_2$$
 $NH_2$ 
 $NH_2$ 

Fig. 2 Reaction of 5-aminotetrazole with lithium hydroxide to form lithium 5-aminotetrazolate

Enthalpy of the reaction illustrated in Fig. 2 is defined by the eqn. (1). Heat of formation at 25 °C of water (-285.8 kJ mol<sup>-1</sup> [18]), lithium hydroxide (-487.5 kJ mol<sup>-1</sup> [18]) and 5-aminotetrazole (5ATZ, 208.64 kJ mol<sup>-1</sup> [19]) are known from the literature. The enthalpy of the reaction was measured using an isoperibolic twin calorimeter (-37.05 kJ mol<sup>-1</sup>) and the enthalpy of formation of lithium 5-aminotetrazolate (LiATZ) calculated from equation (1) as -30.1 kJ mol<sup>-1</sup> (-330.9 kJ kg<sup>-1</sup>).

$$\Delta H_{\rm r} = (\Delta H_{\rm f}({\rm LiATZ}) + \Delta H_{\rm f}({\rm H_2O})) - (\Delta H_{\rm f}({\rm 5ATZ}) + \Delta H_{\rm f.}({\rm LiOH}))$$
 (1)

Sensitivity of lithium salts to impact was determined on a fall hammer apparatus and compared with those of PETN and RDX. Sensitivity curves for the lithium salts LiEDNA, LiTNF and Li<sub>2</sub>TNR and curves for the standard explosives PETN and RDX are presented in Fig. 3, values for 50% probability of initiation summarized in Table 2. Four lithium salts (LiNTO, Li<sub>2</sub>EDNA, LiATZ and LiHexyl) have been evaluated as insensitive compounds; they were not ignited even with impact energy of 98 J (10 kg hammer from 1 m) and hence, they are not covered in Fig. 3. It was shown that the dependence of initiation probability on the impact energy of LiTNF is in a narrow range; therefore, its sensitivity curve is very steep in comparison with curves for other samples. Sensitivity of LiEDNA, LiTNF and Li<sub>2</sub>TNR to impact is significantly lower than the sensitivity of RDX.

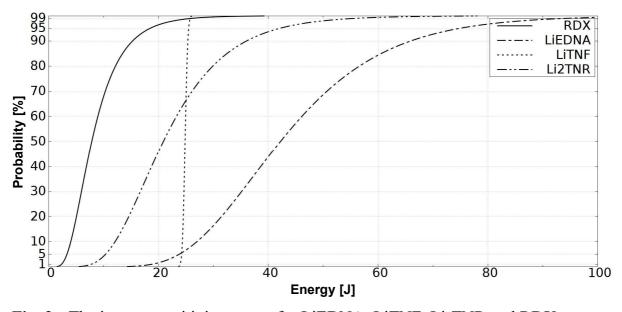
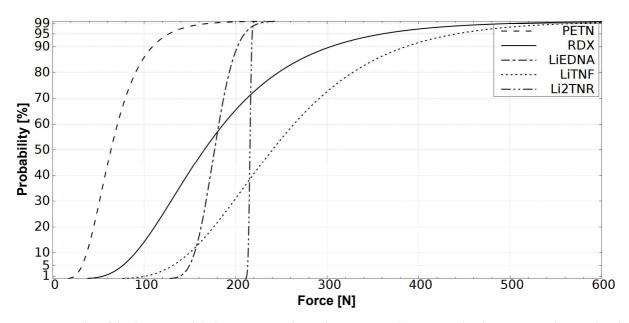


Fig. 3 The impact sensitivity curves for LiEDNA, LiTNF, Li<sub>2</sub>TNR and RDX

Sensitivity to friction was determined on a BAM friction apparatus. Sensitivity curves for LiEDNA, LiTNF and Li<sub>2</sub>TNR and curves for standard explosives PETN and RDX are presented in Fig. 4, values for 50% probability of initiation summarized in Table 2. In the same way as in the case of impact

sensitivity, four lithium salts (LiNTO, Li<sub>2</sub>EDNA, LiATZ and LiHexyl) were evaluated as insensitive compounds. They were not ignited even with a friction force of 360 N. It has been shown that dependence of probability of initiation on friction force of LiEDNA and especially Li<sub>2</sub>TNR is in a narrow range; therefore, the curves for these samples are very steep in comparison with the curves for LiTNF, PETN and RDX. Sensitivities of LiEDNA and Li<sub>2</sub>TNR are roughly on the level of that for RDX (except for the slope of the curves, where LiEDNA and Li<sub>2</sub>TNR are less sensitive at lower friction forces than RDX and more sensitive at the higher friction forces than RDX). Sensitivity of LiTNF is lower than the sensitivity of RDX.



**Fig. 4** The friction sensitivity curves for LiEDNA, LiTNF and Li<sub>2</sub>TNR and standard explosives PETN and RDX

**Table 2** Sensitivity of LiEDNA, LiTNF and Li<sub>2</sub>TNR to impact and friction compared with the sensitivities of PETN and RDX

Compound	Impact energy for 50% probability of initiation [J]	Friction force for 50% probability of initiation [N]
LiEDNA	41.4	177
LiTNF	24.9	240
Li <sub>2</sub> TNR	20.9	216
PETN	_	63.8
RDX	7.9	166

The influence of water of crystalline on sensitivity of explosives is evident in the case of lithium salts of ethylenedinitramine. While Li<sub>2</sub>EDNA forming dihydrate is insensitive to both friction and impact, LiEDNA existing as hemihydrate is sensitive to both stimuli mentioned.

The hygroscopicity of lithium salt was determined by exposure of dry samples at 70% and 90% humidity. The values for a selection of days after exposure are presented in Table 3 and 4. Just two salts appear as hygroscopic at 70% humidity – Li<sub>2</sub>EDNA and LiHexyl. Other lithium salts absorb less than 0.2 % of moisture during 14 days of exposure at 70% humidity. Li<sub>2</sub>EDNA absorbs about 3.7 % during the first day of exposure and then the moisture content stays the same for the remaining days. The most hygroscopic lithium salt, LiHexyl, absorbs 11.0 % of moisture during the first two days of exposure and the sample weight remains the same during the days that follow.

**Table 3** Hygroscopicity of lithium salts and sodium, potassium and ammonium nitrates at 70% humidity

Commound	Hygroscopicity [%] at 70% relative air humidity					
Compound	8 hours	1 day	2 days	7 days	10 days	14 days
KNO <sub>3</sub>	0.0	0.0	0.0	0.0	0.0	0.0
$NaNO_3$	0.0	0.0	0.0	0.0	0.0	0.0
$NH_4NO_3$	0.2	0.7	1.9	7.4	11.4	15.4
LiHexyl	2.7	8.2	11.0	11.0	11.0	11.0
LiNTO	0.1	0.1	0.1	0.1	0.1	0.1
LiEDNA	0.0	0.0	0.0	0.0	0.0	0.0
Li <sub>2</sub> EDNA	1.5	3.8	3.7	3.7	3.7	3.7
Li <sub>2</sub> TNR	0.3	0.3	0.3	0.2	0.2	0.2
LiTNF	0.0	0.0	0.0	0.0	0.0	0.0
LiATZ	0.0	0.0	0.1	0.1	0.1	0.1

However, the 70% humidity level seemed too low for adequate determination of the hygroscopicity of components of pyrotechnic mixtures because both the standards — sodium and potassium nitrates — appear as non-hygroscopic compounds at this humidity level. It is well known that sodium nitrate, unlike potassium nitrate, is quite hygroscopic, which limits its use in many pyrotechnic compositions (e.g. in black powder). Therefore, the measurement at 90% humidity was carried out as well, when the difference between sodium and potassium nitrates was evident. The hygroscopicity of most lithium salts is quite low – they absorb between 1.0 to 3.0 % moisture at 90% humidity during 14 days of exposure.

This means that their hygroscopicity is significantly lower than that of sodium nitrate. The lowest hygroscopicity level was determined for lithium picrate, which does not absorb any moisture during 14 days of exposure at 90% humidity. On the other hand, startlingly high hygroscopicity was found for the lithium salt of 5-aminotetrazole (LiATZ, which had appeared as an almost non-hygroscopic compound at 70% humidity). The hygroscopicity of this salt is almost on the level of ammonium nitrate at 90% humidity. LiHexyl absorbs 11.5 % of moisture during the first day and the weight of the sample then remains almost the same during the days following the start of exposure test.

**Table 4** Hygroscopicity of lithium salts and sodium, potassium and ammonium nitrates at 90% humidity

Commound	Hygroscopicity [%] at 90% relative air humidity					
Compound	8 hours	1 day	2 days	7 days	10 days	14 days
KNO <sub>3</sub>	0.0	0.0	0.0	0.0	0.0	0.0
NaNO <sub>3</sub>	0.0	0.3	0.9	6.3	9.6	15.3
$NH_4NO_3$	1.0	4.6	9.2	28.0	38.7	53.1
LiHexyl	4.4	11.5	11.7	11.6	11.6	11.6
LiNTO	1.4	1.5	1.5	1.5	1.5	1.6
LiEDNA	0.1	0.3	0.5	0.9	1.0	1.7
Li <sub>2</sub> EDNA	0.1	0.2	0.3	0.8	0.7	1.1
Li <sub>2</sub> TNR	2.9	2.8	2.8	2.7	2.7	2.7
LiTNF	0.0	0.0	0.0	0.0	0.0	0.0
LiATZ	0.3	1.9	4.7	21.8	31.8	46.6

#### **Conclusions**

In this work, various lithium salts have been studied. Their preparation was a one-step reaction using lithium hydroxide or lithium carbonate as the source of a lithium cation. Most of the salts investigated form hydrates. Decomposition temperatures determined by DTA are, in most cases, higher than 200 °C and densities vary from 1.7 g cm<sup>-3</sup> to 1.9 g cm<sup>-3</sup>.

The advantage of the lithium salts studied is that they have either low sensitivity (LiEDNA, LiTNF, Li<sub>2</sub>TNR), or are insensitive (LiNTO, Li<sub>2</sub>EDNA, LiHexyl, LiATZ), to both impact and friction. The most promising compound seems to be lithium 5-aminotetrazolate which is insensitive to mechanical stimuli, possesses high nitrogen content, and its preparation is easy.

Enthalpy of formation of lithium 5-aminotetratolate was determined using an isoperibolic twin calorimeter as  $-30.1 \text{ kJ mol}^{-1}$  ( $-330.9 \text{ kJ kg}^{-1}$ ).

#### Acknowledgment

The authors gratefully acknowledge the support of the Ministry of Industry of the Czech Republic (project FV 10332) and Ministry of School and Education of the Czech Republic (project SGS\_2019\_002). We would also like to thank Jaroslav Schuster for graphical processing of impact and friction sensitivity results and to Jakub Šelešovský for useful consultation in the area of calorimetric methods.

#### References

- [1] Kubota N.: *Propellants and Explosives*. Wiley-VCH, Weinheim 2007, pp. 143–148.
- [2] Kubota N.: Determination of plateau burning effect of catalyzed double-base propellant, *Symposium (International) on Combustion* **17**(1) (1979) 1435–1441.
- [3] Hewkin D.J., Hicks, J.A., Powling, J., Watts H.: The combustion of nitric esterbased propellants: ballistic modification by lead compounds. *Combustion Science and Technology* **2** (1971) 307–327.
- [4] Redecker K., Weuter W., Bley U.: Gaserzeugende Mischungen. *DE 19505568* (1996).
- [5] Belov G.V.: RealWin, compute program for calculation of equilibrium characteristics, chemical and phase. Moscow State Technical University and Glushko Thermocenter of the Russian Academy of Sciences, Moscow 1983–2017.
- [6] Koch E.C.: Evaluation of lithium compounds as color agents for pyrotechnic flames. *Journal of Pyrotechnics* **13** (2001) 1–8.
- [7] Koch E.C. Special materials in pyrotechnics: III. Application of lithium and its compounds in energetic systems. *Propellants, Explosives, Pyrotechnics* **29** (2004) 67–80.
- [8] Koch E.C., Jennings-White C.: Is it possible to obtain a deep red pyrotechnic flame based on lithium? in: Klerk W.P.C., van de Lingen J.L. (Eds.): *Proceedings of the 36<sup>th</sup> International Pyrotechnics Seminar 2009 in Rottedram*, International Pyrotechnics Society, Rotterdam 2009, pp. 105–110.
- [9] Ernst V., Klapötke T.M., Stierstorfer J.: Alkali salts of 5-aminotetrazole structures and properties. *Zeitschrift Für Anorganische Und Allgemeine Chemie* **633** (2007) 879–887.
- [10] Zevenbergen J.F., Webb R., Van Rooijen M.P.: Pyrotechnic and fireworks compositions with metal salts of 5-aminotetrazole for colored flames. *WO* 2008127107 (2008).
- [11] Söhnel O., Kroupa M., Franková G., Velich V.: Calcium oxalate crystallization kinetics from calorimetric measurements. *Thermochimica Acta* **306** (1997) 7–12.

- [12] Schuster J., Pelikán V., Selesovsky J.: The new promising test procedure suitable for the energetic materials sensitivity testing, in: Pachman J., Selesovsky J. (Eds): *Proceedings of the 22<sup>nd</sup> Seminar on New Trends in Research of Energetic Materials*, University of Pardubice, Pardubice 2019, pp. 636–641.
- [13] Department of Defense: Method 208.1 Hygroscopicity (Equilibrium method). In *MIL-STD-650 Military standard: Explosive; sampling, inspection and testing*. Department of Defense Armed Forces Support Center. Washington 1962.
- [14] Zhang T.L, Hu R.Z, Liang Y.J, Li F.P: Preparation and mechanism of thermal decomposition of alkali metal (Li, Na and K) salts of 3-nitro-1,2,4-triazol-5-one. *Journal of Thermal Analysis* **39** (1993) 827-847.
- [15] *ICT Database of Thermochemical Values*, version 7.0, Fraunhofer-Institut für Chemische Technologie ICT, Pfinztal 2004 (2004) and references cited therein.
- [16] Tucholski T.: Thermal analysis of picrates. I. Dehydration, melting points and initial and pre-explosive temperatures of lithium, sodium, potassium, rubidium, cesium, copper and silver picrates. *Roczniky Chemii* **13** (1933) 435–447.
- [17] Socrates G.: Infrared and Raman Characteristic Group Frequencies: Tables and Charts. Wiley, Chichester 2011, p. 95.
- [18] Rumble J.J. (Ed.): *Handbook of Chemistry and Physics*, 98<sup>th</sup> Ed., CRC Press, Boca Raton (2017–2018).
- [19] Williams M.M., McEwan W.S., Henry R.A.: The heats of combustion of substituted triazoles, tetrazoles and related high nitrogen compounds. *Journal of Organic Chemistry* **61** (1967) 261–267.