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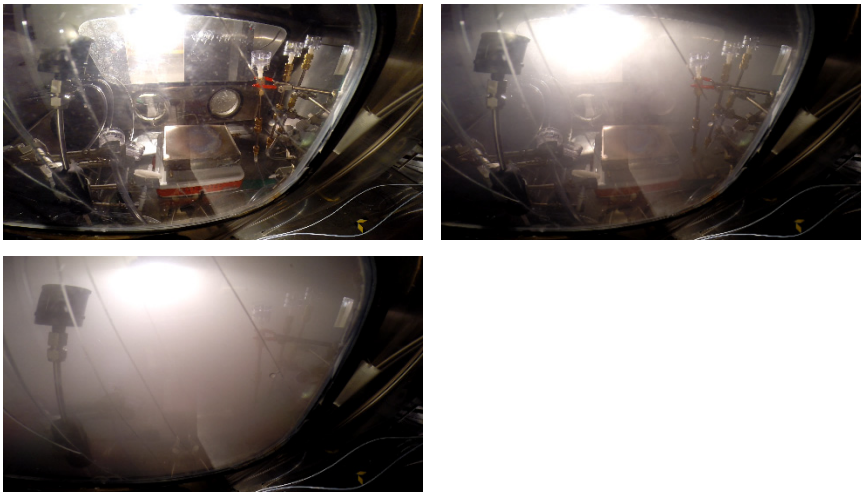
Vented Gases and Aerosol of Automotive Li-ion LFP and NMC Batteries in Humidified Nitrogen under Thermal Load



Titel	Undersökning av ventilerade gaser och aerosoler från litiumjonbatterier av typen LFP och NMC I kvävgasatmosfär
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Cover photo: Gas evolution after thermal runaway and rupture of a Li-ion pouch cell battery

David Sturk, Autoliv Development AB, Sweden

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Sammanfattning

Detta är en studie av ventilerade gaser från litium-jonbattericeller vid termisk rusning i inert atmosfär. Batterier av påscelltyp för bilindustri med litium-järn-fosfat (LFP) och litium-nickel-mangandioxid-kobolt (NMC) katodkemi exponerades för värme i fuktat (motsvarande typisk utomhusmiljö) kvävegasflöde tills dess att cellen sprack p.g.a. invärtes gastryck. Med gaskromatografi-masspektrometri och Fouriertransform infraröd spektroskopi gjordes en skanning av kända och okända substanser. Metalliska grundelement i den partikulära aerosolen analyserades med induktivt kopplad plasma masspektrometri.

Bland de detekterade ämnena finns flera toxiska ämnen, till vår kännedom ej tidigare rapporterade vid ventilering efter termisk rusning. Många av ämnena är irriterande för huden och andningsvägarna. Huruvida de ventilerade gaserna når en exponeringsnivå som kan vara farlig är situationsbunden och slutsatser kring detta kan inte dras i denna rapport. Därför är det viktigt med fullskaliga försök för att utreda exponeringsnivåer för insatspersonal såväl för passagerare i händelse av termisk rusning till följd av exempelvis en krock.

Tre av de detekterade ämnena, etyl etylfosfonofluoridat, etyl metylfosfonofluoridat, och metyl metylfosfonofluoridat har strukturella likheter med kemiska stridsmedel i gruppen organiska fosforföreningar. Uppskattningar av dessa ämnens kvantiteter och eventuella toxicitet vid ett verklighetstroget scenario av en trafikskadehändelse kräver en ny studie med ett större provsystem och mängd provmaterial. Därutöver cellstudier för att studera deras eventuella inhiberingsförmåga av enzymet acetylkolinesteras.

Denna rapport innehåller en förteckning över identifierade kemiska ämnen vid ventilering tillsammans med en toxikologisk verkansbedömning i de fall sådana data finns tillgängliga. Den experimentella uppställningen är beskriven för att på ett säkert sätt kunna utföra dessa studier.

Nyckelord: E-fordon, Litium-jonbatteri, ventilation, gaser, termisk rusning, säkerhet, irriterande ämnen, toxikologisk riskbedömning, LFP, NMC, aerosol

Summary

Chemical compounds were screened in a study on gases ventilated from Li-ion battery cells during thermal runaway in an inert environment. Automotive Li-ion pouch cells of lithium iron phosphate (LFP) and lithium nickel manganese cobalt oxide (NMC) cathode chemistry were exposed to heat-up in humidified nitrogen atmosphere until rupture caused by internally build up pressure. By means of analytic instruments such as Gas Chromatography-Mass Spectrometry and Fourier Transform Infrared Spectroscopy a screening of known and unknown constituent gaseous species was performed. Elemental metal contents in the aerosol phase were analyzed with Inductively Coupled Plasma Mass Spectrometry.

Among the detected compounds there are several, to our knowledge, of potential toxic concern previously not reported to ventilate during thermal runaway of Li-ion batteries. Many of the compounds are irritating to the skin and the respiratory system. Whether the exposure of vented gases reach a dangerous dose in the case of real world accident involving Li-ion batteries cannot be concluded from this study. To assess first responders' occupational exposure risk, as well as victim exposure in e.g. a car accident, a full scale experiment is needed including propagation of thermal runaway in a stack of battery cells.

Three of the detected compounds; ethyl ethylphosphonofluoridate, ethyl methylphosphonofluoridate, and methyl methylphosphonofluoridate are very similar to some organophosphorous chemical warfare agents. However, in order to perform a qualitative estimation of their quantities and possible toxicities in relation to a realistic scenario of a traffic accident, additional studies need to be performed. These include studies on a larger test system and quantity of tested material as well as *in vitro* studies to evaluate if they are potential enzyme inhibitors of acetylcholine esterase. This report includes description of the full experimental setup to safely perform such studies. A list of identified compounds together with toxicological assessment is given.

Keywords: e-vehicle, Li-ion battery, ventilation, gases, thermal runaway, safety, irritating compounds, toxicological assessment, LFP, NMC, aerosol

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1 Introduction

In the event of an E-vehicle crash, quick and competent rescue of the vehicle occupants requires new knowledge and up-dated training to minimize the time to final treatment for those injured. This was the conclusion drawn by the Swedish Civil Contingencies Agency (MSB) in 2011 after analyzing the results of a survey that they had sent out to Swedish first responders. This led to the initiation of a Triple Helix research project, E-Vehicle Safe Rescue (2012-2014), where abusive testing on e-vehicle batteries (cells/modules/packs) were conducted by Swedish partners from the industry, research institutes and academics and the results were compiled by MSB into a free web-based educational material for first responders [Sturk *et al*. 2013]. Amongst mechanical, electrical and thermal abuse tests, bonfire tests on lithium iron phosphate (LFP) and nickel manganese cobalt (NMC) Li-ion battery cells were conducted, analyzed and published [Sturk *et al*. 2015].

In January 2015, MSB identified that a remaining task to be investigated was the composition of gases that can be vented without fire from a critically damaged automotive battery such as the LFP and NMC Li-ion batteries. Those two types of Li-ion batteries were chosen as they are the two most common ones found in commercialized automotive HV batteries. The present study addresses this concern and during autumn of 2015 the Swedish Defense Research Agency (FOI) performed a series of experiments based on battery material provided from E-Vehicle Safe Rescue and Autoliv Development AB.

The results of this investigation will provide MSB with further material to be added to the existing education for first responder rescue routines at the event of a traffic incident involving E-Vehicles.

1.1 Commission

According to quote “FOI-2015-1534 / MSB-2015-09-07”, the team of researchers at FOI were to investigate the ventilated gases from Li-ion pouch cells of the mentioned chemistries by means of Gas Chromatography-Mass Spectrometry (GC-MS) and Fourier Transform Infrared Spectroscopy (FTIR) in order the screen for known and unknown gaseous species. Examples of known gases or vapors that can be generated during critical thermal failure of Li-ion cells are carbon dioxide, carbon monoxide (CO), hydrogen fluoride (HF), fluorocarbons, hydrogen, and vaporized or aerosolized electrolyte alkyd carbonates. [Huang *et al*. 2008, Kawamura *et al.* 2006, Roth, E. P. 2008, Wang *et al.* 2006, Wilken *et al.* 2012, Wilken *et al.* 2013, Yang *et al*. 2006a, Yang *et al*. 2006b, Hammami *et al*. 2003].

The produced scientific report should contain also assessment of which of the identified gases that may result in an intoxication of individuals in the event of a sufficient exposure. The results fulfill requirements set out by MSB.

2 Experimental settings

2.1 Facilities

A 65 m^3 room with stainless steel walls and with air supply from the outside after temperature adjustment and filtered through a particle filter ensured researchers safety. Exhaust air from the steel room passed throw aerosol filters and carbon filters before it was released to the surroundings. Risk assessment prior the experiments demonstrated that the route for exposure was via inhalation and via the skin (particularly HF). To reduce the exposure of toxic compounds a protective mask, protective suit, gloves and boots were worn during critical parts the experiments.

In this room, a glove box was used as test chamber for the thermal challenge of the lithium ion batteries. Inside the glove box a small stainless steel box (referred to as "battery box") was used as a compartment for the lithium ion pouch cell, see figure 1. This glove box of 0.38 m^3 served as a conditioning volume for ventilated gases/aerosol. An exit tube was attached between the glove box and the fan system in order to ventilate the gases and particles after degassing and collection of gases and aerosols.

Figure 1. Battery box with two connections, one for nitrogen gas inlet and one for temperature probe, dimension 204 mm x 264 mm x 64 mm.

Thermal load was applied by an electric resistive heater (simple stove top) until the pouch cell erupted and released hot gases and aerosol. To prevent the emitted gas to take fire experiments were performed in nitrogen atmosphere. It was assumed that when CO_2 decreased to a certain level so had O_2 and the threshold of 15% O_2 to prevent open flame could with excess be fulfilled [Fredholm and Saarkoppel 2012]. Thus O_2 levels were followed indirectly by studying CO_2 level evolution on GASMET after the glove box was sealed and evacuated by inserting N_2.

Dry nitrogen was moistened with water (MilliQ) to 63% RH (20 g H_2O /h at 30 l/min N_2 which corresponds to 11 g water/m^3 at 20°C) to simulate typical outdoor climate. Nitrogen humidification was done with a Controlled Evaporator Mixer, type W-300 and a mini CORI-FLOW digital Mass Flow meter (Bronkhorst High-Tech B.V., NL), figure 2. The nitrogen flow to the Mixer was set with a mass flow controller (0-100 L/min). The humidified nitrogen flow was connected to the battery box. Temperatures inside the battery box and the glove box were measured with thermocouples connected to two handheld TESTO 435-4 instruments (Testo inc. Germany) connected to laptops for data logging. To monitor the battery box inside the glove box during the experiments, one digital video action camera (GoPro 3) was used, with Wi-Fi the recording pictures could be seen on the screen of a connected cellular phone. See the glove box with sampling equipment in figures 3 and 4.

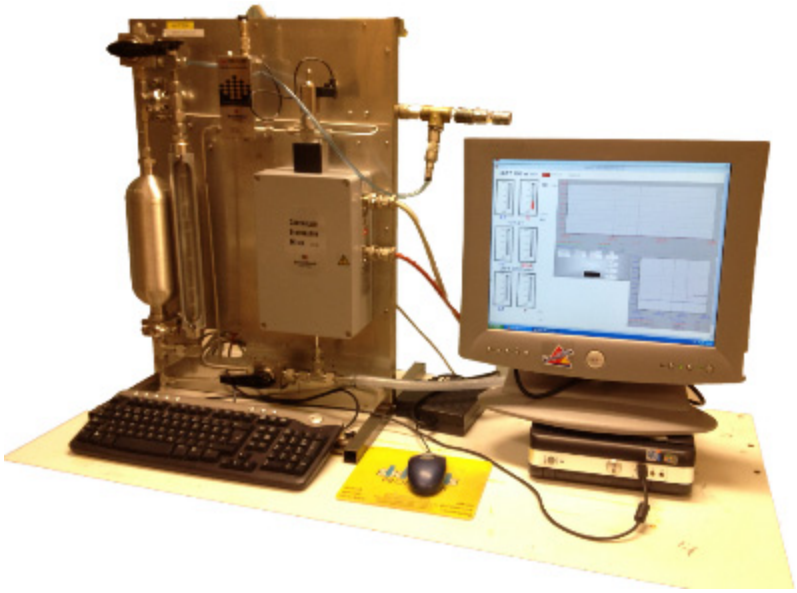


Figure 2. A mass flow controller and a humidifier were used to supply the battery box with humidified nitrogen.

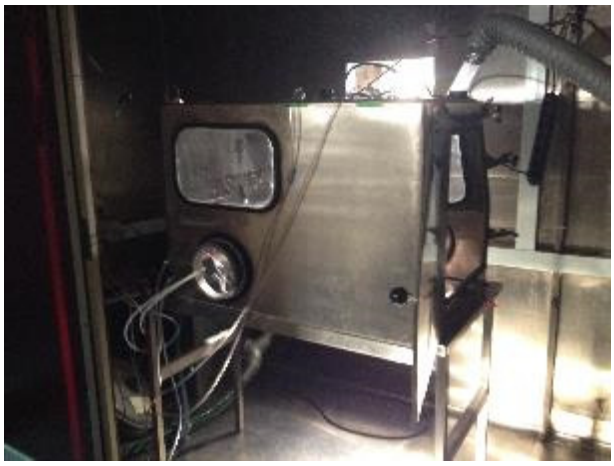


Figure 3. The glove box of 0.38 m^3 used to condition vented gases and aerosols.

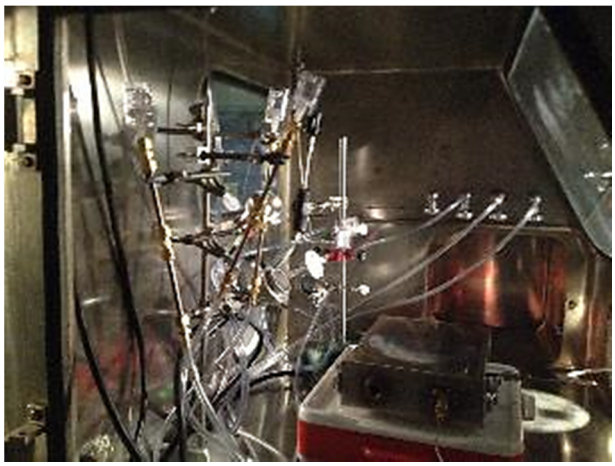


Figure 4. Inside the glove box with all sampling equipment setup and the battery box on the heater ready to receive thermal load until ventilation.

2.2 Sampling methods and analysis protocol

2.2.1 Filter and adsorbents

Air sampling with Tenax tube (PerkinElmer, USA), Carbosieve tube (PerkinElmer, USA) and 25 mm GF filter (PALL, USA), connected to a sampling train, was done with PocketPump's (SKC inc., USA) at a flowrate of 100 mL/min. The GF filter was used to protect the gas sampling tubes of Carbosieve and Tenax. The sampled air passed the Tenax tube first, removing semi volatile compounds, volatile compounds passed the Tenax tube and were collected on the Carbosieve tube. Particulate aerosols were collected on 37 mm PVC filter (PALL, USA) and a set of 47 mm GF filter and an Anasorb 747 adsorbent tube. The sampling rate for the PVC filter was 5 L/min (Leland Legacy pump, SCK inc, USA) and 2 L/min for the 47 mm GF filter with Anasorb 747 tube (AirCheck2000, SKC inc.).

2.2.2 GC-MS

The adsorbent tubes (Tenax and Carbosieve) were analysed by thermal desorption gas chromatography (TD-GCMS). The instrumentation used were TD: TurboMatrix 350 ATD, Perkin Elmer; GC: Agilent 7890A Gas Chromatograph; MS: Agilent 5975C MSD. Adsorbent tubes were desorbed at 250°C during 3 min using a split ratio of 1:10 (inlet split 200 mL/min, tube desorb 20 mL/min). The cold trap used to refocus the analytes was set to 2°C for Tenax adsorbent tubes using a Thermal Desorber Trap, Packed with Tenax (M041-3535, Perkin Elmer, CT, USA). The analytes from the Carbosieve adsorbent tubes were refocused onto an Air Monitoring Trap (M041-3628, Perkin Elmer, CT, USA) kept at a temperature of -30°C. After the initial desorption stage the trap was rapidly heated to 250°C to introduce the analytes to the GC after a second split of 1:10. The temperature of the valve and transfer line were 180°C and 200°C respectively. Chromatographic separation was performed using DB-5 MS analytical column (Agilent J&W scientific, USA) with a length of 30 m x 0.25 mm and a film thickness of 0.25 µm. The GC profile was as follows: initial temperature was kept at 40°C for 1 min, then increased to 100°C at a rate of 5°C/min and then ramped at 15°C/min until 300°C. The mass spectrometer was operated in full scan mode (mass 29-400) to allow identification. Samples were quantified against calibrations generated using toluene in methanol spiked onto an adsorption tube. The raw data files were evaluated using the software AMDIS.

2.3 Metal analysis

The aerosol sample collected on PVC-filter were dissolved using a microwave oven and HNO_3 / HF in a Teflon vessels. The metal analyses (elements) were performed with ICP-SFMS according to EN 17294 to 1.2 (modified) and EPA Method 200.8 (modified) by ALS Scandinavia, Sweden.

2.3.1 FT-IR

During the experiments gas measurements were done with two FTIR (Fourier transform infrared spectroscopy) instruments, a GASMET model DX-4030 instrument (Gasmet Technologies OY, Finland) and a Bruker Alpha instrument with a 5 cm gas cell (Bruker Corporation, Germany). Of particular interest are volatile gases that do not adsorb onto the Carbosieve tubes; HF and CO. HF has a rotational-vibrational structure in the region 3600 to 4200 cm^{-1}. The P-branch is interfered by overlapping water signal and only the R-branch (> 4000 cm^{-1}) can be used. Due to the longer path length GASMET analyzer was found best for low ppm levels. HF reference spectra and a method based on the only the R-branch was used

to study HF. CO has absorptions at 2114 cm^{-1} and 2180 cm^{-1} (NIST) and is predesigned gas in the library of GASMET.

Bruker Alpha was used together with a 5 cm optical path length gas cuvette. 16 scans with double-sided forward-backward collection in repeated mode measurements. Background was taken as the heat was started. The spectral window was extended to 5000 cm^{-1} to accommodate possible HF absorptions.

2.4 Test procedure

The empty battery box was conditioned at over 250 °C to degas possible interfering substances. Background measurements were done with an empty battery box in a similar fashion as sharp measurements. Totally four experiments were done with two types of Li-ion batteries, two with single LFP pouch cells and two with single NMC pouch cells; referred to as LFP1 (3.2 V), LFP2 (3.26 V), NMC1 (3.84 V), and NMC2 (3.84 V).

The battery was placed inside the battery box. Amounts of degassed substance was determined from battery weights before and after the experiment. To prevent the plastic casing of the battery pouch cell to glue onto the surface of the battery box during the thermal release an alumina foil was placed between the battery and the box. A perforated metal U-profile clamped between the battery and the ceiling of the battery box prevented the battery to swell in the middle and ensured optimal thermal connection.

The battery box was closed and placed on the electric heater, and nitrogen supply and the temperature probe was connected. Air samplers were placed inside the glove box, tubings to the FTIR instruments were connected and a temperature probe was connected to the glove box. The door to the glove box was closed and the humidified nitrogen flushed the glove box until the carbon dioxide concentration inside the glove box was reduced to a low value (< 1/3 of initial concentration).

The battery box was heated until the release of aerosol to the glove box. At that sign the power to the heater was shut down. Sampling started immediately and proceeded 10 min. On the first run (LFP1), it was discovered that gas concentrations inside the glove box were too high for GASMET as its spectra were saturated. The sampled gas to the instrument was then diluted 100 times with a Dekati dubble diluter (Dekati Ltd, Finland).

Following the 10 min, the humidification of nitrogen ended and the nitrogen flow increased to 50 L/min to evacuate the glove box to minimize the risk of open flame as the door is opened and volatile electrolyte gases is exposed to oxygen in surrounding air.

After about another 10 min the glove box was visually clear and filter and adsorbents were collected and sealed.

Between the experiments the battery box and glove box was cleaned with moistened paper towels.

3 Results

3.1 Thermal runaway

The pouch cells ruptured on the long sides as opposed to the weakest point which was anticipated to be around the tabs, figure 5. For the gas evolution this was not of any concern.

The temperature evolution inside the battery box is shown in figure 6. Heating of the battery box also created a small temperature rise inside the glove box, figure 7.

The humidity inside the battery box and inside the glove box were not recorded by a humidity sensor but can be estimated from the absolute humidity of 11 g H_2O/m^3 and the recorded temperatures in the battery box. At the maximum temperatures recorded during thermal runaway this corresponds to < 1% RH in all four experiments. In the glove box on the other hand humidities were between 7.9% RH at 46 °C and 11% RH at 39 °C.

Figure 5. Ruptured pouch cell of LFP type. NMC type is similar.

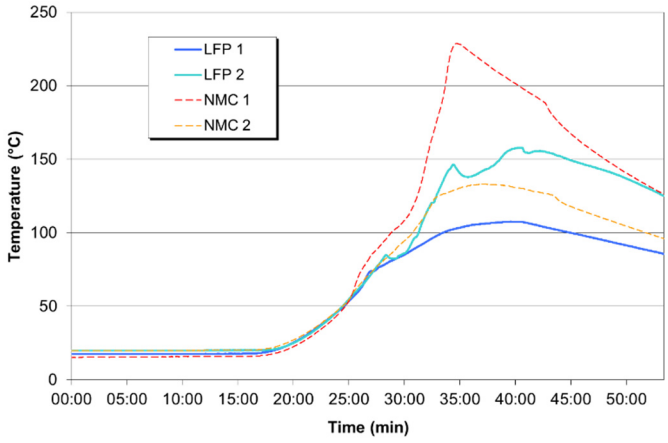


Figure 6. Temperatures inside the battery box. We emphasize that temperature evolution inside the battery box may well dependent on how the pouch opened relative the position of temperature measurement head and when the heater is powered off.

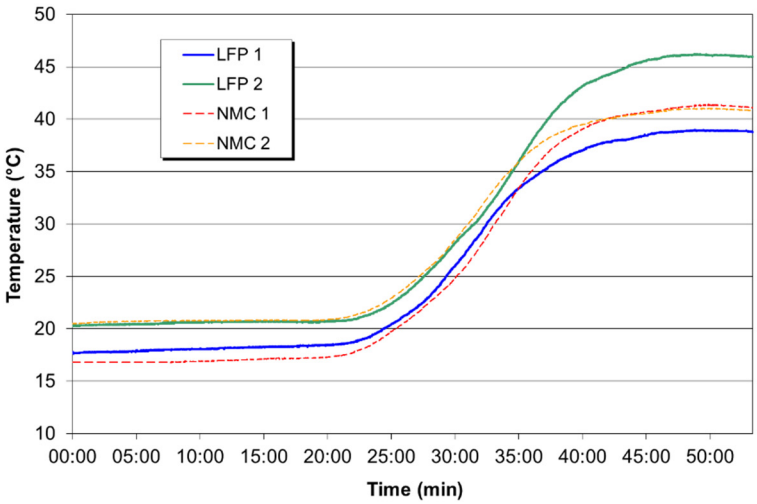


Figure 7. Temperatures inside the glove box.

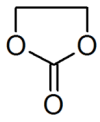
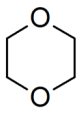
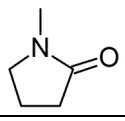
3.2 Chemical analysis

Substances identified from adsorbent tubes by means of ATD-GCMS are summarized in table 1 and 2 for LFP and NMC batteries respectively. Compounds were identified using the software AMDIS (Automated Mass spectral Deconvolution and Identification System). The selection criteria for a positive identification was a match factor above 90.

The most abundant compounds emitted from the batteries were carbonates. Diethyl carbonate (DEC) and ethylmethyl carbonate (EMC) found in the LFP battery and dimethyl carbonate (DMC) and EMC in the NMC battery. In addition, both battery types contained large amounts of 1,3-dioxolan-2-one.

Similar compounds are detected for the different battery types. However, in the NMC batteries phosphonofluoridates were detected which were not found in the LFP batteries. The volatile compounds previously reported with FT-IR such as phosphorylflouride, pentafluorophosphate and hydrogenfluoride were not detected in our experiment. Notably is that a sweet smell occurred after ventilation, even though high safety precautions were taken in the setup to avoid exposure.

Table 1. Compounds emitted from LFP battery.

Chemical compound	Structure	CAS#	Concentration (µg/m^3)
1,3-dioxolan-2-one		96-49-1	300
1,4-dioxane		123-91-1	0.2
1,4-oxathiane		15980-15-1	10
1-methylpyrrolidin-2-one		872-50-4	5

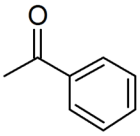
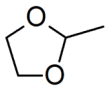
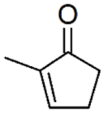
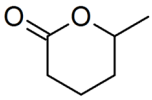
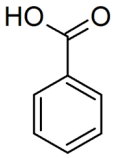
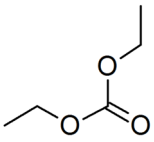
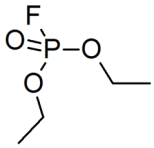
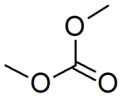
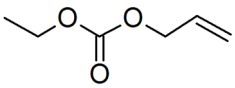
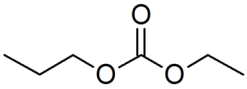
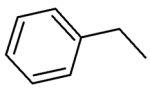
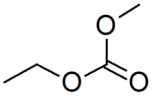
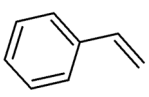
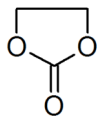
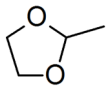
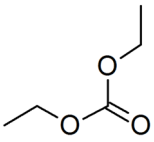
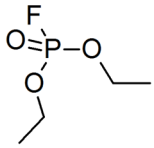
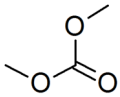
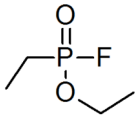
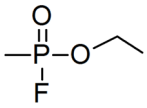
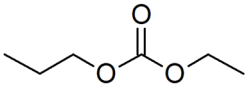
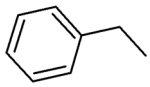
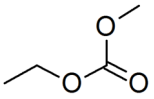
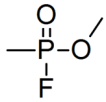
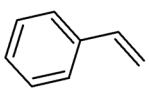
Chemical compound	Structure	CAS#	Concentration (µg/m^3)
1-phenylethanone		98-86-2	1
2-methyl-1,3-dioxolane		497-26-7	2
2-methylcyclopent-2-en-1-one		1120-73-6	0.2
6-methyloxan-2-one		823-22-3	0.1
Benzoic acid		65-85-0	0.1
Diethyl carbonate (DEC)		105-58-8	1000
Diethyl phosphorofluoridate		358-74-7	0.5
Dimethyl carbonate (DMC)		616-38-6	1
Ethyl prop-2-enyl carbonate		1469-70-1	0.1
Ethyl propyl carbonate		35363-40-7	0.1
Ethylbenzene		100-41-4	2
Ethylmethyl carbonate (EMC)		623-53-0	1000
Styrene		100-42-5	5

Table 2. Compounds emitted from NMC battery.

Chemical compound	Structure	CAS#	Concentration (µg/m^3)
1,3-dioxolan-2-one		96-49-1	100
1,4-oxathiane		15980-15-1	2
2-methyl-1,3-dioxolane		497-26-7	10
Diethyl carbonate (DEC)		105-58-8	30
Diethyl phosphorofluoridate		358-74-7	10
Dimethyl carbonate (DMC)		616-38-6	300
Ethyl ethylphosphonofluoridate		650-20-4	0.2
Ethyl methylphosphonofluoridate		673-97-2	0.5
Ethyl propyl carbonate		35363-40-7	0.01
Ethylbenzene		100-41-4	0.1
Ethylmethyl carbonate (EMC)		623-53-0	1000
Methyl methylphosphonofluoridate		353-88-8	0.02
Styrene		100-42-5	5

3.3 Metal analysis and Total Suspended Particles (TSP)

In order to investigate the presence of metal compounds emitted from the batteries, ICP-MS analysis was performed on two filters (one replicate) for each trial. Although filters clogged after a few minutes of sampling because of the dense aerosol, concentrations could still be retrieved because pumps recorded sampled volume. Of special interest were lithium and cathode elements such as manganese, cobalt and nickel. The variation between sample and replicate is large and for many elements one of the samples were below the detection limit of the method. As the primary interest is to indicate any presence of metal element, the highest levels for each battery type is reported in table 4. Also blank levels (empty glove box) show that the experiment setup release metals, note that blank levels are subtracted in table 4. Many of the selected elements are present in the aerosol. To our knowledge this is the first report on metal contents of vented aerosols from Li-ion batteries.

LFP
Interestingly lithium was detected in the LFP batteries but not in the NMC batteries. Trial LFP2 had the highest lithium levels of 46 µg/m^3. Nickel, cobalt, and manganese were found in both battery types at lower levels (see also toxicological assessment below). Note that LFP batteries were prior to NMC to avoid contamination of the setup.

NMC
High concentrations of TSP are found in all trials and NMC types seems to release more particles than LFP. Averages of the two sample heads in each trial are reported in table 3. The between trial variation is large, from 1.4 g/m3 for LFP1 to 7 g/m3 for NMC1. The amount released range from 30 to 49 g and follow TSP values with NMC > LFP.

The intact cells are of similar weights within the same type of cell. NMC batteries are heavier than LFP (386 vs. 236 g).

Table 3. Elements detected by ICP-MS, background from glove box subtracted. TSP values are averages of the two sample heads in each trial. Released amounts are calculated from weights before and after thermal runaway.

Element (down)	Trial (right)	LFP1	LFP2	NMC1	NMC2
TSP*	g/m^3	1.4	5.3	7.0	5.3
Released amount	g	30	43	49	46
Co	µg/m3	0.036	0.11	0.39	0.016
Li	µg/m3	2.2	46	n.d.	n.d.
Mn	µg/m3	1.2	1.5	2.8	1.1
Ni	µg/m3	0.24	1.2	1.1	1.8
Pb	µg/m3	1.5	0.21	0.09	0.31
Sn	µg/m3	6.8	1.8	0.37	2.0

*TSP, Total Suspended Particles
n.d. not detected

3.4 FT-IR

Spectra contain in general many absorptions in the fingerprint region, figure 8, and in the high-wavenumber region, figure 9. Many of these are absorptions likely from electrolyte vapors, see ref [Wilken *et al.* 2012]. Of special interest are gases that are not readily collected onto the gas adsorbents. Previously known compounds are POF_3 and PF_5 [Yang *et al.* 2006b]

which are intermediates in HF evolution. However, none of these can readily be assigned from IR spectra. Particularly a peak at 989 cm^{-1} has previously been assigned to the asymmetric stretch of P-F of POF_3 [Yang *et.al.* 2006b] but since spectra lack P=O stretch at 1415 cm^{-1} as well as the symmetric P-F stretch mode 873 cm^{-1} we do not infer any POF_3 from IR spectra. Similar observations are made for PF_5. Absorptions in the IR spectra in the region 940-1040 cm^{-1} are thus likely to originate from other fluorophosphorous compounds. It is known that both POF_3 and PF_5 have their major evolution between 170°C and 200°C [Wilken *et al*. 2012] which is over the measured temperature in the battery box for three of four trials. Whether this is the cause of their absence is beyond the scope of this study.

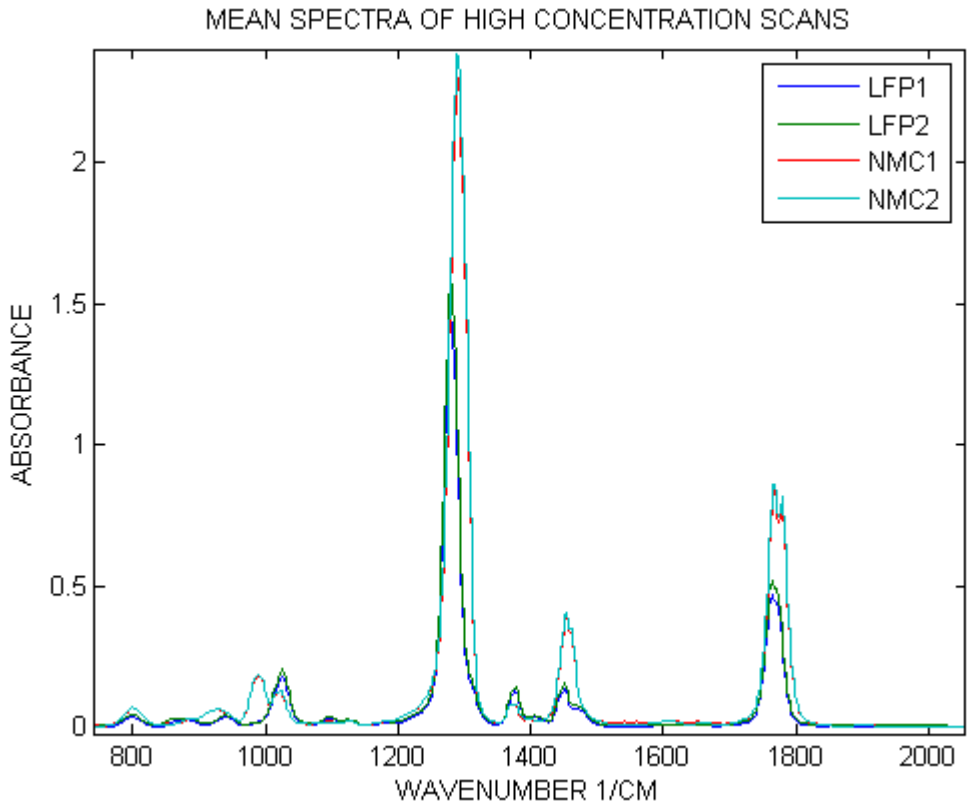


Figure 8. FT-IR spectra of the fingerprint region.

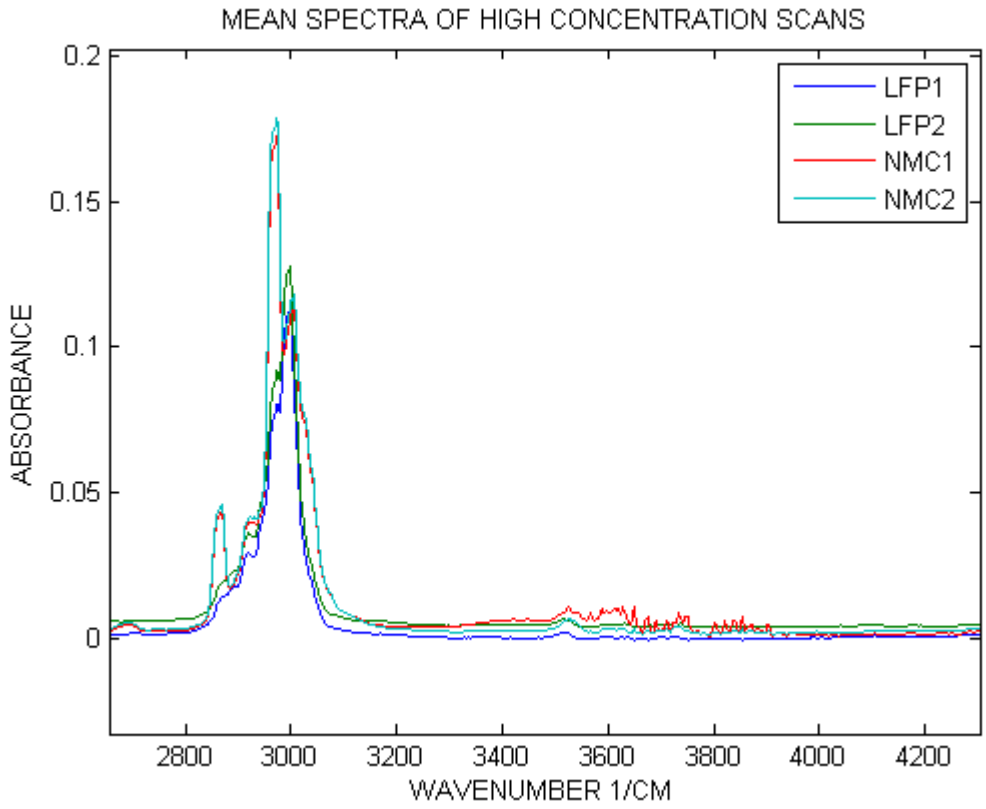


Figure 9. FT-IR spectra of the high-wavenumber region.

Only for trial LFP1, positive HF signal could be inferred from GASMET analyzer. This is because this trial was run without sample dilution and hence chances are greatest to observe HF. Qualitative agreement is found, however, there is an interfering signal that makes quantitative assignment ambiguous. With the current method levels are indicated at ~50 ppm at maximum for LFP1. Other trials (LFP2, NMC1, and NMC2) the sample gas were diluted with air 1:100 and no HF could be detected. Dräger tubes were co-deployed (without dilution) and repeated use show that HF levels varied rather quickly over the battery ventilation, with highest levels measured in the early stage of ventilation. Possibly because of the time-point of sampling, the highest levels of HF was found for NMC cells and numbered >200 ppm. CO is analyzed at 2114 and 2180 cm^{-1}[http://webbook.nist.gov/]. There is no evidence found of CO in FT-IR spectra. Due to budget/time limitations no effort has been done for a full spectral band assignment, but table 4 of found absorptions is included for future reference.

Table 4. Infra-red absorption bands of vented gases for both LFP and NMC battery types. Strength is subjective.

Wavenumber cm^{-1}	Type (B=both)	Strength
799	B	w
928	NMC	vw
942	LFP	vw
989	NMC	m
1024-1028	B	m
1097	B	vw
1126	B	vw
1280	LFP	vs
1289	NMC	vs
1371	B	w
1379	B	w
1444	LFP	w
1452	LFP	w
1454	NMC	m
1463	NMC	m
1764	LFP	s
1769	NMC	s
1779	NMC	s
1773	LFP	s
2109	NMC	vw
2211	NMC	vw
2342	B	m
2362	B	m
2866	NMC	w
2968	NMC	m
2972	LFP	w
2996	LFP	m
3005	NMC	w
3515	LFP	m
3523	NMC	m
3600-4000	B	m
4451	LFP	w
4453	NMC	w

vw – very weak
w – weak
m – medium
s – strong
vs – very strong

3.5 Toxicological assessment

The overall goal is to evaluate health risks during rescue in case of thermal runaway of automotive Li-ion batteries. The present experiments have detected a complex mixture of organic chemicals and metals emitted from two battery chemistries of automotive Li-ion pouches. The following summary gives a first indication of potential hazards related to single exposures via air to these chemicals but cannot fully take into account the possible consequences of mixed exposures. Most gaseous compounds are detected in low concentrations during heating of one battery pouch. However, the values for total suspended particles are well above limit level value for total dust (5 mg/m^3). To evaluate the relation between concentrations in air and risk for toxic effects during rescue, a full scale experiment is necessary. For several of the detected substances there were no or very little toxicological data available in the databases used in this overview.

In brief, several of the chemicals are mildly to severely irritating to the eyes, respiratory tract and to the skin. For instance, both ethylbenzene and styrene are harmful to the airways. Hydrogen fluoride is corrosive and may cause serious systemic intoxication after inhalation or skin exposure. Also lithium induces corrosive effects to both the skin and respiratory system.

Lithium levels are above the ceiling limit value in this experimental setup for one trial (LFP2). Other metal elements analyzed are far below the level limit value. It should however be noted that the current metal analysis does not include measurements of their physical and chemical properties which could highly affect the potential for toxic effects. Manganese, for instance, is considered more neurotoxic when in an ionic state as compared to large particles.

Several chemicals can be taken up by the skin, including 1,4-dioxane, ethylbenzene, styrene, 1-methylpyrrolidin-2-one and cobalt. Of these, two of the chemicals, 1,4-dioxane and cobalt, are classified by the Swedish Work Environment Authority as carcinogens.

Three of the chemicals are phosphonofluoridates or phosphorofluoridates. Their structural similarity to some organophosphorus compounds (e.g. nerve agent sarin) indicate that they potentially could be highly toxic. The first step to evaluate if these chemicals may cause toxicity would be to analyze their potential to inhibit the enzyme acetylcholinesterase. If these chemicals can inhibit the enzyme to a relevant degree this should be followed by an *in vitro* screening of medical countermeasures.

Table 5. Toxicological assessment

Chemical compound	CAS no.[1]	TOXNET[2] Skin eyes, respiratory tract	Hygienic limit values[3]	Labelling of chemicals according to ECHA[4]: Hazard codes for chem-phys & human health
1,3-dioxolan-2-one	96-49-1	Irritating to eyes, skin and airways.	---	NA
1,4-dioxane	123-91-1	Very irritating to eyes, skin and airways. Possibly carcinogenic. LC_{50} mice inhalation. 37 g/m^3/2 h LC_{50} rats inhalation. 46 g/m^3/2 h	Limits (1996) LLV 35 mg/m^3 TV 90 mg/m^3 (H) The substance can easily be absorbed through the skin. (C)The substance is carcinogenic	Highly flammable liquid and vapour (H225), Causes serious eye irritation (H319), May cause respiratory irritation (H335), Suspected of causing cancer (H351), May form explosive peroxides (EUH019), Repeated exposure may cause skin dryness or cracking (EUH066)
1,4-oxathiane	15980-15-1	NA	---	# Flammable liquid and vapour (H226), Causes skin irritation (H315), Causes serious eye irritation (H319) May cause respiratory irritation (H335)
1-methylpyrrolidin-2-one	872-50-4	Irritating to eyes and skin. Headaches and chronic eye irritation have been reported at levels of 2.9 g/m^3.	Limits (2015) LLV 40 mg/m^3 STV 80 mg/m^3 (H) The substance can easily be absorbed through the skin. (R) The substance may impair fertility.	Causes skin irritation (H315), Causes serious eye irritation (H319), May cause respiratory irritation (H335), May damage fertility or the unborn child (H360D)
1-phenylethanone	98-86-2	Irritating to eyes and skin	---	Harmful if swallowed (H302), cause serious eye irritation (H319)
2-methyl-1,3-dioxolane	497-26-7	Induce muscle weakness LC_{50} mice inhalation.:59 g/m^3 LC_{50} rats inhalation.:80 g/m^3 (ChemIDplus)	---	# Highly flammable liquid and vapour (H225), Causes serious eye irritation (H319).

Chemical compound	CAS no.[1]	TOXNET[2] Skin eyes, respiratory tract	Hygienic limit values[3]	Labelling of chemicals according to ECHA[4]: Hazard codes for chem-phys & human health
2-methylcyclopent-2-en-1-one	1120-73-6	NA	---	# Flammable liquid and vapour (H226)
6-methyloxan-2-one	823-22-3	NA	---	# Causes serious eye irritation (H319)
Benzoic acid	65-85-0	Vapours may induce irritation to eyes, skin and airways. (Mild irritant)	---	Causes skin irritation (H315), Causes serious eye damage (H318), Causes damage to the lungs through prolonged or repeated exposure (H372)
Cobolt (Co)	7440-48-4	Cough, shortness of breath, wheezing, asthma. May induce itching at skin exposure.	Group limit values (2011) LLV Inhalable dust 0.02 mg/m^3 (C) The substance is carcinogenic (H) The substance can easily be absorbed through the skin. (S) The substance is sensitizing.	May cause an allergic skin reaction (H317). May cause allergy or asthma symptoms or breathing difficulties if inhaled (H334)
Diethyl phosphofluoridate	358-74-7	An organophosphoruschemical. Old studies indicate that the chemical is toxic after exposure via skin or inhalation (ChemIDplus).	---	NA
Diethylcarbonate (DEC)	105-58-8	Very irritating to eyes, skin and airways.	---	# Flammable liquid and vapour (H226)
Dimethyl carbonate (DMC)	616-38-6	Irritating to eyes, skin and airways. LD_{50} rats inhalation. ≥14 mg/m^3/4h	---	Highly flammable liquid and vapour (H225)
Ethyl ethylphosphonofluoridate	650-20-4	NA, but is an organophosphorus chemical	---	NA

Chemical compound	CAS no.[1]	TOXNET[2] Skin eyes, respiratory tract	Hygienic limit values[3]	Labelling of chemicals according to ECHA[4]: Hazard codes for chem-phys & human health
Ethyl methylphosphonofluoridate	673-97-2	NA, but is an organophosphorus chemical	---	NA
Ethyl prop-2-enyl carbonate	1469-70-1	NA	---	Flammable liquid and vapor (H226), Causes skin irritation (H315), Causes serious eye irritation (H319)
Ethyl propyl carbonate	35363-40-7	NA	---	NA
Ethylbenzene	100-41-4	Irritating to eyes, skin and mucous.	Limits (2015) LLV 220 mg/m^3 STV 884 mg/m^3 (H) The substance can easily be absorbed through the skin.	Highly flammable liquid and vapor (H225), May be fatal if swallowed and enters airways (H304), Harmful if inhaled (H332), May cause damage to organs (hearing) (H373)
Ethylmethyl carbonate (EMC)	623-53-0	NA	---	# Flammable liquid and vapor (H226), Causes skin irritation (H315), Causes serious eye irritation (H319), May cause respiratory irritation (H335)
Hydrogen fluoride (HF)	7664-39-3	Highly toxic and highly corrosive. Dermal exposure leads to severe burns. HF is adsorbed through skin. Inhalation can lead to pulmonary edema and pneumonia. Skin or inhalation may provide high risk of hypocalcemia.	Limits (2015) NGV 1.5 mg/m^3 STV 1.7 mg/m^3 For exposure to a mixture of fluorides and hydrogen fluorides, the level limit value for fluorides shall be applied.	Fatal if swallowed (H300), Fatal in contact with skin (H310), Causes severe skin burns and eye damage (H314), Fatal if inhaled (H330)

Chemical compound	CAS no.[1]	TOXNET[2] Skin eyes, respiratory tract	Hygienic limit values[3]	Labelling of chemicals according to ECHA[4]: Hazard codes for chem-phys & human health
Lead (Pb)	7439-92-1	Both skin and respiratory exposure can lead to systemic effects including effects on the nervous system (CDC). Suspected carcinogen.	Group limit value (2011) LLV Inhalable dust 0.1 mg/m^3 Respirable dust 0.05 mg/m^3 (B) Exposure approaching existing professional hygienic limit values and simultaneous exposure to noise levels approaching the action value of 80 dB can cause damage to hearing. (M) Medical supervision may be required for handling of this substance. (R) The substance may impair fertility.	NA
Lithium (Li)	7439-93-2	Corrosive with risk for serious effects on eyes, skin and mucus. Risk for oedema and corrosive damage on the respiratory tract.	Group limit value (2011) STV Inhalable dust 0,02 mg/m^3	In contact with water releases flammable gases which may ignite spontaneously (H260), Reacts violently with water (EUH014), Causes severe skin burns and eye damage (H314)
Manganese (Mn)	7439-96-5	Can be neurotoxic chemical	Group limit values (2000) NGV Total dust 0.2 mg/m^3 Respirable dust 0.1 mg/m^3	NA
Methyl methylphosphonofluoridate	353-88-8	NA, but is an organophosphorus chemical	---	NA

Chemical compound	CAS no.[1]	TOXNET[2] Skin eyes, respiratory tract	Hygienic limit values[3]	Labelling of chemicals according to ECHA[4]: Hazard codes for chem-phys & human health
Nickel (Ni)	7440-02-0	Nickel may sensitization of the skin.	Group limit value (1978) LLV Total dust 0.5 mg/m^3 (S) The substance is sensitizing.	Refers to dust of nickel (<1mm in diameter) May cause an allergic skin reaction (H317), Suspected of causing cancer (H351), Causes damage to organs through prolonged or repeated exposure (H372)
Styrene	100-42-5	Irritating to eyes, skin and mucous. Health effects include changes in color vision, fatigue, reduced alertness, concentration and balance.	Limits (2011) LLV 43 mg/m^3 STV 86 mg/m^3 (H) The substance can easily be absorbed through the skin. (B)Exposure approaching existing professional hygienic limit values and simultaneous exposure to noise levels approaching the action value of 80 dB can cause damage to hearing. (M) Medical supervision may be required for handling of this substance.	Flammable liquid and vapor (H226), Causes skin irritation (H315), Causes serious eye irritation (H319), Harmful if inhaled (H332), Suspected of damaging fertility or the unborn child (H361d), Causes damage to organs (hearing) (H372)
Tin (Sn)	7440-31-5	Irritating to eyes, skin and respiratory system.	Group limit value (2011) LLV Inhalable dust 2 mg/m^3	NA

Footnotes and affiliations, see next page.

[1]CAS no.: Chemical number according to Chemical Abstract Service

[2]TOXNET: Toxicology data network at NIH (http://toxnet.nlm.nih.gov/). The Hazardous Substances Data Bank was used as the database if not otherwise stated. The information presented here focuses on toxicity after exposure via the skin, respiratory tract and eyes.

[3]Hygienic limit values. Information from (www.av.se; AFS 2015:7 in Swedish).

[4]Labelling according to CLP. Information from ECHA (http://.echa.europa.eu/). Labelling of chemical, physical and human health hazards are presented giving an indication of possible effects.

[#] The chemical does not have a harmonized classification and labelling. Labelling is presented in the table when most companies have registered the same phrases.

LD_{50}: Lethal dose where 50% of the individuals die.

LC_{50}: Lethal concentration where 50% of the individuals die.

LLV: Level limit value (Nivågränsvärde in Swedish).

STV: Short-term value (Korttidsvärde in Swedish). These values are used for toxic chemicals that do not have Ceiling limit values.

NA: Not available

4 Discussion and conclusion

Among the detected compounds there are several, to our knowledge, of toxic concern previously not reported to ventilate during thermal runaway of Li-ion batteries. Many of the compounds are irritating to the skin and the respiratory system. Whether the exposure of vented gases reach a dangerous dose in the case of real world accident involving Li-ion batteries cannot be concluded from this study. To assess first responders' occupational exposure risk, as well as victim exposure in e.g. a car accident, a full scale experiment is needed including propagation of thermal runaway in a stack of battery cells.

Furthermore, three of the detected compounds; ethyl ethylphosphonofluoridate, ethyl methylphosphonofluoridate, and methyl methylphosphonofluoridate are structurally very similar to the chemical warfare agent sarin but as previously stressed, their real toxicity in a realistic e-vehicle traffic accident scenario cannot be estimated based on the present study. Studies should be conducted to determine if these affect the neurotransmitter regulator enzyme acetylcholinesterase and until then extra attention should be paid.

Also the reverse is true, previously reported PF_5, POF_3, $POF(OH)_2$, $POF_2(OCH_2CH_2)_nF$, and POF_2OMe [Wilken *et al*. 2012, Wilken *et al*. 2013, Grutzke *et al*. 2015] as well as 2-fluoroethanol and bis-(2-fluoroethyl)-ether [Hammami *et al*. 2003] are not observed here. This study is a pilot study of an entire pouch cell in humidified nitrogen atmosphere whereas previous studies focus on isolated systems of electrolyte and/or electrode materials. This may explain the difference in observed compounds, and the reaction pathways outlined [Wilken *et al*. 2013] may not necessarily be very different from this study.

Some unforeseen problems in the project were encountered. Breakthrough of carbonates from Tenax to Carbosieve adsorbents made the analysis of smaller gaseous compounds such as HF, PF_5, and POF_3 cumbersome. Luckily, FT-IR is a technique suited to study these compounds. Time evolution of IR spectra has not been studied here but it is something that would gain further insight in the evolution pathway chemistry.

We experienced this project to be too small for a satisfactory and full chemical analysis of ventilated Li-ion batteries. This included as full spectral assignment of vibrational modes in FT-IR spectra, time-evolution analysis of the same, adsorbent sampling separating on volatility to avoid contaminating Carbosieve adsorbent, and analysis of TSP fraction with regards to less volatile organic and in-organic contents.

We did learn some good lessons from the experimental work. Because of the complex environment we recommend specific sensor for certain compounds, e.g. HF and CO. Online FT-IR measurements (GASMET) can be used to indirect (by CO_2 declination) monitor oxygen levels to avoid open flame of the vented gases. Last, FT-IR spectral changes was the first indicator of chemical emitted from battery ventilation, before any greater amount of visual smoke.

5 Literature cited

Fredholm Lotta, Saarkoppel Fredrik. In Swedish. Sänkt syrehalt förebygger bränder. BrandSäkert, 2012, Vol.7 pp. 28-30, www.brandsakert.se

Grutzke M., Kruger S., Kraft V., Vortmann B., Rothermel S., Winter M., Nowak S.,Investigation of the Storage Behavior of Shredded Lithium-Ion Batteries from Electric Vehicles for Recycling Purposes. ChemSusChem, 2015. 8(20): p. 3433-8.

Hammami Amer, Raymond Nathalie and Armand Michel. Runaway risk of forming toxic compounds. Nature, 2003, Vol. 424, pp. 635-636.

Huang Qian, Yan Manming and Jiang Zhiyu. Thermal study of organic electrolytes with fully charged cathodic materials of lithium-ion batteries. J. Solid State Electrochem., 2008, Vol. 12, pp. 671-678. DOI 10.1007/s10008-007-0400-7.

Kawamura Tetsuya, Okada Shigeto and Yamaki Jun-ichi. Decomposition reaction of LiPF6-based electrolytes for lithium ion cells. J. of Power Sources, 2006, Vol. 156, pp. 547-554.

Roth E. P. Abuse Response of 18650 Li-Ion Cells with Different Cathodes Using EC:EMC/LiPF6 and Screening of Vented Gases and Aerosols from Li-Ion LFP and NMC Batteries under Nitrogen atmosphere EC:PC:DMC/LiPF6 Electrolytes., ECS Translations, 2008, Vol. 11, pp. 19-41.

Sturk David, Hoffman Lars. In Swedish. E-fordons Potentiella Riskfaktorer vid en Trafikskadehändelse. 2013, Rapport från FFI projektet Räddningskedjan. Available at http://e-fordon.blogspot.se/.

Sturk David, Hoffmann Lars and Tidblad Annika Ahlberg. Fire tests on E-Vehicle Battery Cells and Packs. Traffic Injury Prevention. Feb 25, 2015.

Wang Qingsong, Sun Jinhua, Yao Xiaolin, Chunhua Chen., Micro calorimeter study on the thermal stability of lithium-ion battery electrolytes. J. of Loss Prevention in the Process Industries, 2006, Vol. 19, pp. 561-569. doi: 10.1016/j.jlp.2006.02.002.

Wilken Susanne, Treskow Marcel, Scheers Johan, Johansson Patrik and Jacobsson Per, Initial stages of thermal decomposition of LiPF6-based lithium ion battery electrolytes by detailed Raman and NMR spectroscopy. RSC Advances, 2013, Vol. 3, pp. 16359-16364.

Wilken Susanne, Johansson Patrik and Jacobsson Per. Infrared spectroscopy of instantaneous decomposition products of LiPF6-based lithium battery electrolytes., Solid State Ionics, 2012, Vol. 225, pp. 608-610.

Yang Hui *et al*., A Review of Li-Ion Cell Chemistries and their Potential use in Hybrid Electric Vehicles., J. Ind. Eng. Chem., 2006a, Vol. 12, pp. 12-38.

Yang Hui, Zhuang Guorong V and Ross Jr. Philip N. Thermal stability of LiPF6 salt and Li-ion battery electrolytes containing LPF6., J. of Power Sources, 2006b, Vol. 161, pp. 573-579. doi: 10.1016/j.jpowsour.2006.03.058.