



## Two-dimensional ion chromatography for the separation of ionic organophosphates generated in thermally decomposed lithium hexafluorophosphate-based lithium ion battery electrolytes



Vadim Kraft, Martin Grützke, Waldemar Weber, Jennifer Menzel, Simon Wiemers-Meyer, Martin Winter, Sascha Nowak\*

University of Münster, MEET Battery Research Center, Institute of Physical Chemistry, Corrensstraße 46, 48149 Münster, Germany

### ARTICLE INFO

#### Article history:

Received 8 April 2015

Received in revised form 22 June 2015

Accepted 13 July 2015

Available online 16 July 2015

#### Keywords:

Two-dimensional ion chromatography

Heart-cutting mode

Ionic organophosphates

Electrospray ionization mass spectrometry

Inductively coupled plasma mass spectrometer

Lithium ion battery electrolytes

### ABSTRACT

A two-dimensional ion chromatography (IC/IC) technique with heart-cutting mode for the separation of ionic organophosphates was developed. These analytes are generated during thermal degradation of three different commercially available Selectilyte™ lithium ion battery electrolytes. The composition of the investigated electrolytes is based on 1 M lithium hexafluorophosphate (LiPF<sub>6</sub>) dissolved in ethylene carbonate/dimethyl carbonate (50:50 wt%, LP30), ethylene carbonate/diethyl carbonate (50:50 wt%, LP40) and ethylene carbonate/ethyl methyl carbonate (50:50 wt%, LP50). The organophosphates were pre-separated from PF<sub>6</sub><sup>-</sup> anion on the low capacity A Supp 4 column, which was eluted with a gradient step containing acetonitrile. The fraction containing analytes was retarded on a pre-concentration column and after that transferred to the high capacity columns, where the separation was performed isocratically. Different stationary phases and eluents were applied on the 2nd dimension for the investigation of retention times, whereas the highly promising results were obtained with a high capacitive A Supp 10 column. The organophosphates generated in LP30 and LP40 electrolytes could be separated by application of an aqueous NaOH eluent providing fast analysis time within 35 min. For the separation of the organophosphates of LP50 electrolyte due to its complexity a NaOH eluent containing a mixture of methanol/H<sub>2</sub>O was necessary. In addition, the developed two dimensional IC method was hyphenated to an inductively coupled plasma mass spectrometer (ICP-MS) using aqueous NaOH without organic modifiers. This proof of principle measurement was carried out for future quantitative investigation regarding the concentration of the ionic organophosphates. Furthermore, the chemical stability of several ionic organophosphates in water and acetonitrile at room temperature over a period of 10 h was investigated. In both solvents no decomposition of the investigated analytes was observed and therefore water as solvent for dilution of samples was proved as suitable.

© 2015 Elsevier B.V. All rights reserved.

### 1. Introduction

The lithium-ion battery (LIB) technology is considered as one of the key technologies of the 21st century. Applications for LIBs include portable devices like smartphones, camcorders and mp3 players as well as stationary energy storage systems and electric vehicles [1]. In order to develop a sustainable mobility, LIBs are one of the most promising mobile energy storage technologies [2]. Despite the advantages of LIBs like high power, low self-discharge and long cycle life, several challenges including limited energy

density, still improvable safety and aging behavior of the battery compounds remain, to improve LIB performance [3]. The mechanisms of aging are not yet completely understood or verified. For example, there are various different processes in the LIB that are made responsible for the loss of capacity [4]. Moreover, aging is a strongly temperature dependent phenomenon since e.g. the used conducting salt LiPF<sub>6</sub> is not thermally stable and begins to decompose even at about 60 °C reacting with the electrolyte solvents like ethylene carbonate (EC) and dimethyl carbonate (DMC) [5,6]. In this case, among various decomposition products, non-ionic [5,7,8] and ionic [8–10] organophosphates are formed as reported in previous works. These studies were performed at 60–85 °C, which is above the usual operating temperatures of the batteries. Systematic investigations of the temperature influence on the formation of

\* Corresponding author. Tel.: +49 2518336735; fax: +49 251 83 36032.  
E-mail address: [sascha.nowak@uni-muenster.de](mailto:sascha.nowak@uni-muenster.de) (S. Nowak).

the organophosphates were not carried out, so far. As reported, the presence of several organophosphates at already 60 °C was registered [5,6]. Furthermore, high temperatures can be achieved, e.g. at accidents (thermal runaway) of the electric vehicles using lithium ion batteries.

Some products such as methyl fluorophosphate (MFP) have P–F bonds in their structure, which brings up questions about their toxicity. For example, the neurotoxin diisopropyl fluorophosphate is known for its high toxicity as a consequence of the reaction with the enzyme acetylcholinesterase [11]. The acetylcholine is an important neurotransmitter in autonomic and central nerve systems of mammals. After the transmission of a nerve impulse the acetylcholine is metabolized by acetylcholinesterase. The nerve agents irreversibly bind this enzyme, which leads to the accumulation of acetylcholine causing death at high concentrations [12]. The investigation of LIB electrolyte decomposition products is therefore important for an improvement of the LIB cycle life as well as potentially toxicological aspects.

There are numerous literature reports about the detection of these organophosphates. Identification of the resulting analytes was carried out with nuclear magnetic resonance spectroscopy (NMR), which allowed the detection of ionic as well as neutral compounds [5,7,13]. Furthermore, the application of gas chromatography–mass spectrometry (GC–MS) and high resolution-electrospray ionization–mass spectrometry (HR-ESI-MS) in positive mode is known for the investigation of neutral organophosphates [14–17,30]. A trendsetting method for the detection of organophosphates with low temperature plasma ambient ionization high resolution mass spectrometry (LTP-HR-MS) working in positive and negative mode was reported by Vortmann et al. [8]. The authors identified dimethyl fluorophosphate (DMFP) in positive mode and MFP in positive as well as in negative mode.

Several organophosphates have a P–OH bond which allows the use of ion chromatography (IC) for the investigation of the ions, as was illustrated by our previous works [9,10,18]. By use of this technique the ionic organophosphates were not only detected in the thermally decomposed samples, but also in electrolytes from field tested commercially available batteries [19]. In all cases the co-elution and low retention on the A Supp 4 column of the organophosphates was observed, complicating the elucidation of the structures and also making it impossible to quantify them with conductivity detection [9]. This challenge motivated us to develop and apply a two dimensional ion chromatography (IC/IC) method which is presented in this work.

On the one hand, IC/IC opens a variety in application of different eluents which allows solving even very difficult separation problems. On the other hand, it is a demanding method due to the complexity of the setup. In general, there are two main methods to transfer the analytes from the first to the second dimension: the heart-cutting and the comprehensive mode [20]. Beside two columns, the first method requires a pre-concentration column. The fraction with the analytes is transferred from the first dimension on the pre-concentration column and then onto the second dimension, on which the separation occurs. An important condition is the use of chemical suppression since the eluent from the first column must be deactivated. Furthermore, the flow rate for the second dimension is independent of the first which makes this method relatively flexible. The application of the heart-cutting method was used for example for the analysis of perchlorate in drinking water or HF determination [20–24]. The second method differs insofar that not some specific fractions but the complete eluent is transferred onto the second column. The transfer is achieved in fractions what requires the use of an eight-way valve [25]. The flow rate of the second dimension must be much higher compared the first dimension; also the use of a gradient is important [26]. Johns et al. applied

comprehensive IC/IC with a gradient-pulse column switching for the separation of 18 inorganic anions by a short analysis time [27].

In this study, we developed and applied a two dimensional IC method for the complete separation of organophosphates generated in thermally decomposed LiPF<sub>6</sub>-based organic carbonate solvent LIB electrolytes. Due to the co-elution of our analytes which is happening on a defined section of the first dimension and because of the application of chemical suppression in our setup, the heart-cutting mode using an ion pre-concentration column was chosen for the separation (see Fig. S1). The organophosphates were pre-separated from PF<sub>6</sub><sup>−</sup> and after pre-concentration time transferred to the 2nd dimension. Moreover, the phosphorous selective determination of the analytes was performed by hyphenation of the IC/IC to inductively coupled plasma mass spectrometry (ICP-MS).

## 2. Experimental

### 2.1. Chemicals

Battery grade SelectiLyte™ electrolytes (BASF, Ludwigshafen, Germany) were used as received. The LP30 electrolyte consists of 1 M LiPF<sub>6</sub> in ethylene carbonate/dimethyl carbonate (EC/DMC) (50/50 wt%), the LP40 electrolyte consists of 1 M LiPF<sub>6</sub> in ethylene carbonate/diethyl carbonate (EC/DEC, 50/50 wt%) and the LP50 electrolyte consists of 1 M LiPF<sub>6</sub> in ethylene carbonate/ethyl methyl carbonate (EC/EMC, 50/50 wt%). Deionized water for the preparation of eluents, standard solutions and dilution of analytes was produced with a Milli-Q water system using a LC-PAK cartridge (Bedford, USA). Sodium carbonate (Certipur®) and sodium bicarbonate (for analysis) for IC measurements were purchased from Merck (Darmstadt, Germany). Sodium hydroxide containing eluents were prepared with 50% NaOH (EMSURE®) solution (Merck, Darmstadt, Germany). For the thermal aging experiments, 10 ml aluminum vials with butyl/polytetrafluoroethylene (PTFE) caps were used (Leicht & Appel GmbH, Bad Gandersheim, Germany). Methanol and acetonitrile (both HPLC gradient grade) were ordered from VWR (Bruchsal, Germany). Isopropanol (EMSURE®, 99.9% purity, for analysis) was purchased from Merck (Darmstadt, Germany). Dibutyl phosphate (DBP) (97.0% purity) was ordered from Sigma–Aldrich (Steinheim, Germany).

### 2.2. IC/IC conditions

All ion chromatographic investigations were carried out with instruments of Metrohm (Herisau, Switzerland). An 850 Professional IC with conductivity detection was used for 1st dimension separation. For the 2nd dimension, a conductivity detector and two 872 extension modules with an additional pump, a chemical suppressor and a CO<sub>2</sub> suppressor were applied. The samples were injected with an 889 IC sample center. The IC systems were controlled with the software MagIC Net 3.0 (Metrohm, Herisau, Switzerland). For all separation experiments on the 1st dimension, aqueous solutions of 1.8/1.7 mmol Na<sub>2</sub>CO<sub>3</sub>/NaHCO<sub>3</sub> or 9 mM NaOH and a gradient step with acetonitrile were applied (0–10 min: 1.8/1.7 mmol Na<sub>2</sub>CO<sub>3</sub>/NaHCO<sub>3</sub>). The percentage of acetonitrile was changed as follows: 0 min, 0%; 10 min, 0%; 12 min, 50%; 19 min, 50%; 20 min, 0%; 30 min, 0%.

The experiments on the 2nd dimension were carried out isocratically. For investigation of analyte stabilities in solvents, the method using Metrosep A Supp 7-250/4.0 column with a flow of 0.7 ml/min, an aqueous solution of 4.5/4.25 mmol Na<sub>2</sub>CO<sub>3</sub>/NaHCO<sub>3</sub> and a gradient step were applied: 0 min, 25%; 9 min, 25%; 12 min, 45%; 20 min, 45%; 21 min, 25%; 30 min, 25%. Further information including the used columns and applied parameters are presented in Table S1.

Download English Version:

<https://daneshyari.com/en/article/1199008>

Download Persian Version:

<https://daneshyari.com/article/1199008>

[Daneshyari.com](https://daneshyari.com)