

## Application News

HIC-ESP Ion Chromatograph

### Analysis of Ionic Compounds in Recycled Lithium-Ion Battery Material

Waldemar Weber<sup>1</sup>, Vadim Kraft<sup>1</sup>  
1 Shimadzu Europa GmbH

#### User Benefits

- ◆ A routine and fast IC method for analysis of ionic compounds in „black mass“
- ◆ Monitoring of the recycling quality
- ◆ Quantitative analysis of remaining ions in LIB black mass

#### ■ Introduction

The increasing reliance on lithium-ion batteries (LIB), primarily due to the rise of electric vehicles and portable electronics, has brought about significant environmental concerns regarding their recycling. Toxic heavy metals, organic solvents and plastic are unwanted environmental contaminants. Furthermore, the materials such as lithium, cobalt, nickel, copper, organic carbonates are very valuable if their recycling is properly managed. The recycling process is complex and not widely implemented, leading to a loss of valuable resources and contributing to the demand for new raw materials. Moreover, improper disposal can result in hazardous chemical releases, posing health risks to communities and ecosystems. To address these issues, advancements in recycling technologies are crucial. Developing efficient methods for extracting and reusing materials from spent batteries can mitigate environmental impacts and reduce the carbon footprint associated with battery production.

A typical intermediate product of LIB recycling is the so called „black mass“. Within this application, we demonstrate a very easy and reliable analytical method utilizing IC technology to investigate and to quantify the ionic compounds in a black mass for quality control of a special „hydro washing“ recycling process.

#### ■ Sample preparation

One gram of each sample was placed in 50 mL PP tubes, filled to 50 mL mark with ultrapure water and ultrasonicated within 30 min. Thereafter, vials were centrifuged 10 min at 4500 rpm and 2 mL aqueous phase was filtrated through 0.2 µm PES syringe filters into 1.5 mL PP sample injection vials.

#### ■ Method details

An ion chromatography system HIC-ESP of Shimadzu (Fig. 1) was used for analysis. The analytical conditions are listed in Tab. 1.



Figure 1: Shimadzu HIC-ESP ion chromatograph

Table 1: Analytical conditions

IC instrument	HIC-ESP
IC parameter	Column
	Shim-pack IC-SA2 with SA2(G)
	Column temperature
	25 °C (28 °C conductivity cell)
IC parameter	Flow rate
	1 ml/min
IC parameter	Eluent
	1.8 mmol/L Na <sub>2</sub> CO <sub>3</sub> / 1.7 mmol/L NaHCO <sub>3</sub>

#### ■ Formation mechanism of ionic compounds in recycled material

The formation of ionic compounds during the recycling process follows same reaction sequence as the formation during the native aging of the battery. A high temperature and typical presence of water significantly accelerate the degradation of LiPF<sub>6</sub> salt. Therefore, the expected content of ionic compounds in the recycled material is much higher in comparison to a very old LIB electrolyte. The formation starts from an equilibrium  $\text{LiPF}_6 \rightleftharpoons \text{PF}_5 + \text{LiF}$ . Under reaction with water and the first destruction product POF<sub>3</sub>, the follow up reactions up to the formation of phosphoric acid can be observed in dependence of the degradation grade. The formation mechanism is summarized in Fig. 2.

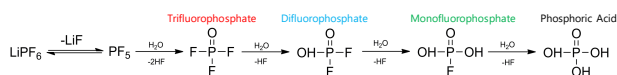


Figure 2 : Formation mechanism of major ionic compounds at the recycling process

In addition, the reactivity of P–F–based species leads to the formation of organo-ionic compounds as a parallel reaction. The structural composition of such compounds is dependent on the organic carbonates in the respective electrolyte. Due to a much lower reactivity of organic carbonates in comparison to water, the content of such species is in the trace range. In all black mass samples shown in this application, a high sulfate content was detected. The source for the sulphate may be the destruction of sulfur-based additives (e.g. 1,3-propane sultone) or alternatively the used sulfuric acid during the recycling process, which can be used to increase the effectivity of heavy metals extraction.

## ■ Qualitative analysis of black mass

The three available black mass samples from one supplier were measured with IC using the method conditions shown in Tab 1. The qualitative composition of samples is nearly identical. The obtained chromatogram is shown in Fig. 3.

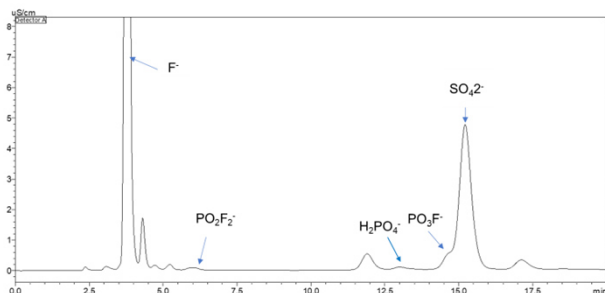


Figure 3: Chromatogram of a black mass sample with identified compounds

The largest observed peak can be clearly identified as fluoride. According to the mechanism shown in the Fig. 1, this is an expected result. The second large compound, identified as sulfate, is typically not present in aged LIB electrolyte. Here we assume, the conditions at the recycling process itself are the source for its formation. Typical degradation products  $\text{PO}_2\text{F}_2^-$ ,  $\text{PO}_3\text{F}^-$  and  $\text{H}_2\text{PO}_4^-$  are present in minor amounts. Peak on the right side of the fluoride at 3.5 min is typically the mixture of organic P-based ions. Other species could not be identified. Black mass as a mixture of all kind of different batteries may include smaller content of salts different from  $\text{LiPF}_6$  as well.

## ■ Quantitative analysis of black mass

As shown in the chromatogram in Fig. 3,  $\text{PO}_3\text{F}^-$  is coeluting with sulfate peak, therefore in this special case a quantification is not possible. In addition,  $\text{PO}_2\text{F}_2^-$  can potentially be quantified using external calibration, nevertheless due to its extreme reactivity any reliable quantitation can not be fulfilled. In this application we consider only  $\text{F}^-$ ,  $\text{SO}_4^{2-}$  and  $\text{H}_2\text{PO}_4^-$  as candidate for an accurate quantitation. The external calibration curves (5-100 ppm) for fluoride and phosphate are shown in the Figure 4. The calculated  $R^2$  value was for all three compounds  $>0.999$ .

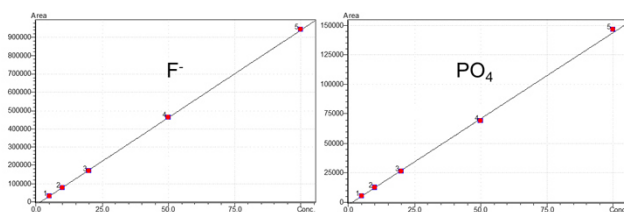


Figure 4: Calibration curves for fluoride and phosphate used for quantification

In case the analysis should not be very accurate, e.g. just to confirm the content below, one point calibration using a standard mixture is a suitable alternative to the calibration curves, making the analysis to a very simple procedure.

Fluoride, phosphate and sulfate were quantified in three samples. The main ionic compounds are in the range of g/kg. The obtained results are summarized in Tab. 2. The high measured content of sulfate makes the theory of its source from additives unrealistic, most probably it is the recycling process with sulfuric acid. In reverse, a high content of fluoride is explainable, a typical LIB (the full assembly) based on

Table 2: Quantitative values of ions detected in black mass

Compound	Sample 1	Sample 2	Sample 3
Fluoride	5.8 g/kg	7.6 g/kg	9.5 g/kg
Phosphate	0.4 g/kg	1.1 g/kg	1.1 g/kg
Sulfate	4.7 g/kg	4.5 g/kg	6.5 g/kg

As the exact conditions of the "hydro washing" recycling and the differences between the samples 1 to 3 are not known, any further interpretation of the results is not possible.

## ■ Conclusion

The presented application demonstrated the suitability of ion chromatography to investigate the extraction processes and the purification of black mass. The final reuse of this product in LIBs is strongly dependent on its purity. Ionic species like sulfate will decrease its capacity and durability. Utilizing the ion chromatography a screening of the purity can be realized on a very simple way, at the same the method is suitable to support the optimization process for the recycling procedures.