

Analysis of Ionic Compounds in Recycled Lithium-Ion Battery Material

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1. 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.



2. Experimental part

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.

Analytical conditions

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



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)
	Flow rate	1 ml/min
	Eluent	1.8 mM Na ₂ CO ₃ / 1.7 mM NaHCO ₃
	Detection	Suppressed conductivity

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 accelerate the destruction of LiPF₆ salt many times over. 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 POF₃, the follow up reactions up to the formation of phosphoric acid can be observed in dependence of the destruction grade. The formation mechanist is summarized in Figure 1.

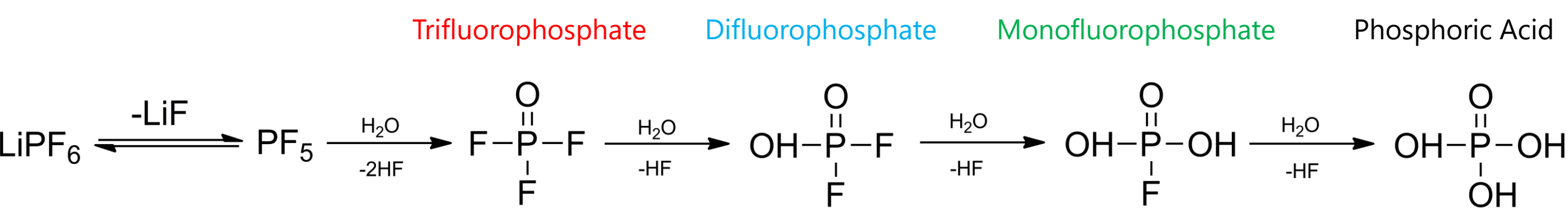


Figure 1: Formation mechanism of major ionic compounds at the recycling process

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 sufur-based additives (e.g. 1,3-propane sultone) or alternatively the used sulfuric acid during the recycling process, which is can be used to increase the effectivity of heavy metals extraction.

2. Results

Qualitative analysis of black mass

The three available black mass samples from one supplier were measured with IC using the method conditions shown in Table 1. The qualitative composition of samples is nearly identical. The obtained chromatogram is shown in Figure 2.

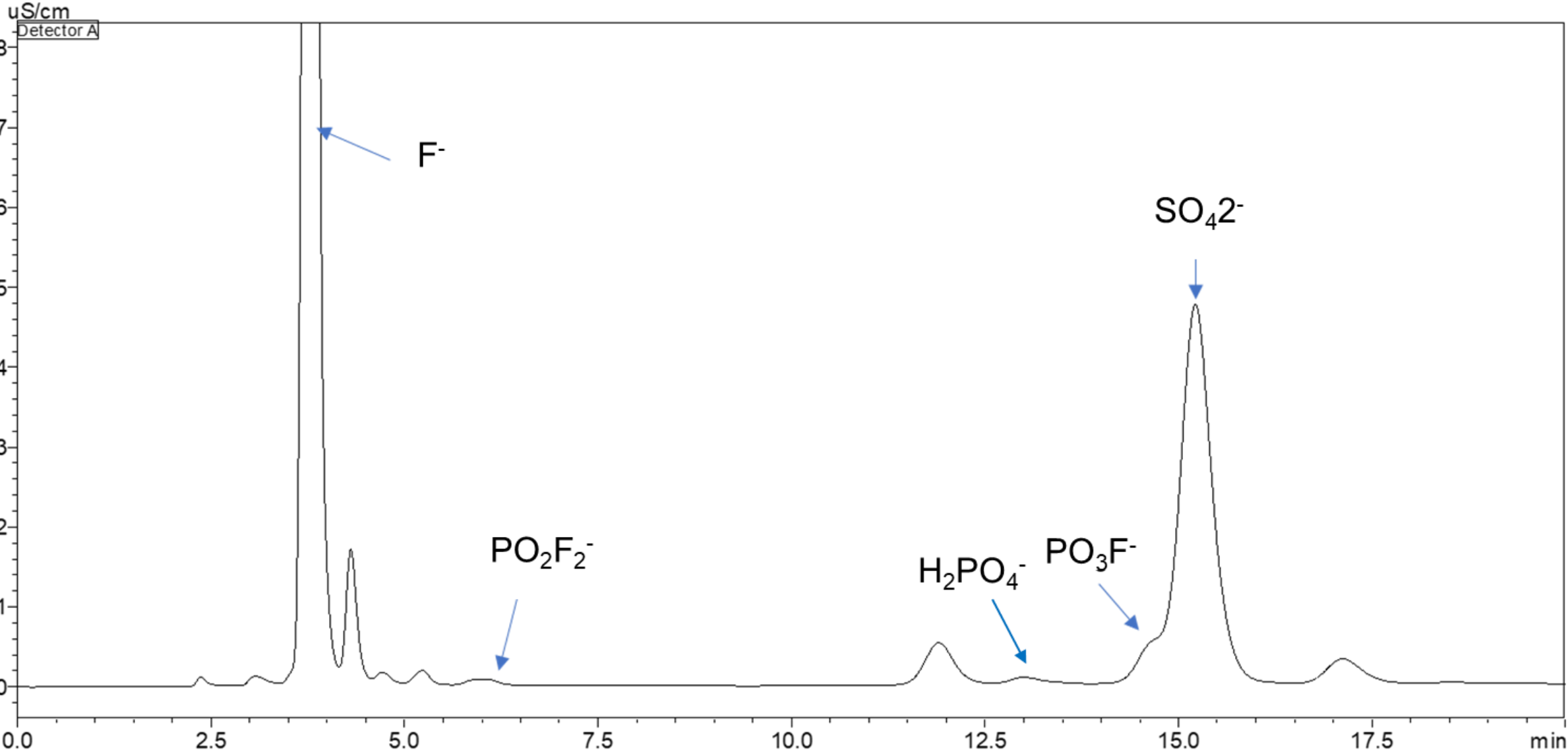


Figure 2: Chromatogram of a black mass sample with identified compounds

The largest observed peak can be clearly identified as fluoride. According to the mechanism shown in the Figure 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 PO₂F₂⁻, PO₃F⁻ and H₂PO₄⁻ 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 LiPF₆ as well.

Quantitative analysis of black mass

As shown in the chromatogram Figure 2, PO₃F⁻ is coeluting with sulfate peak, therefore in this special case a quantification is not possible. In addition, PO₂F₂⁻ 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 F⁻, SO₄²⁻ and H₂PO₄⁻ as candidate for an accurate quantitation. The external calibration curves (5-100 ppm) for fluoride and phosphate are shown in the Figure 3. The calculated R² value was for all three compounds >0.999.

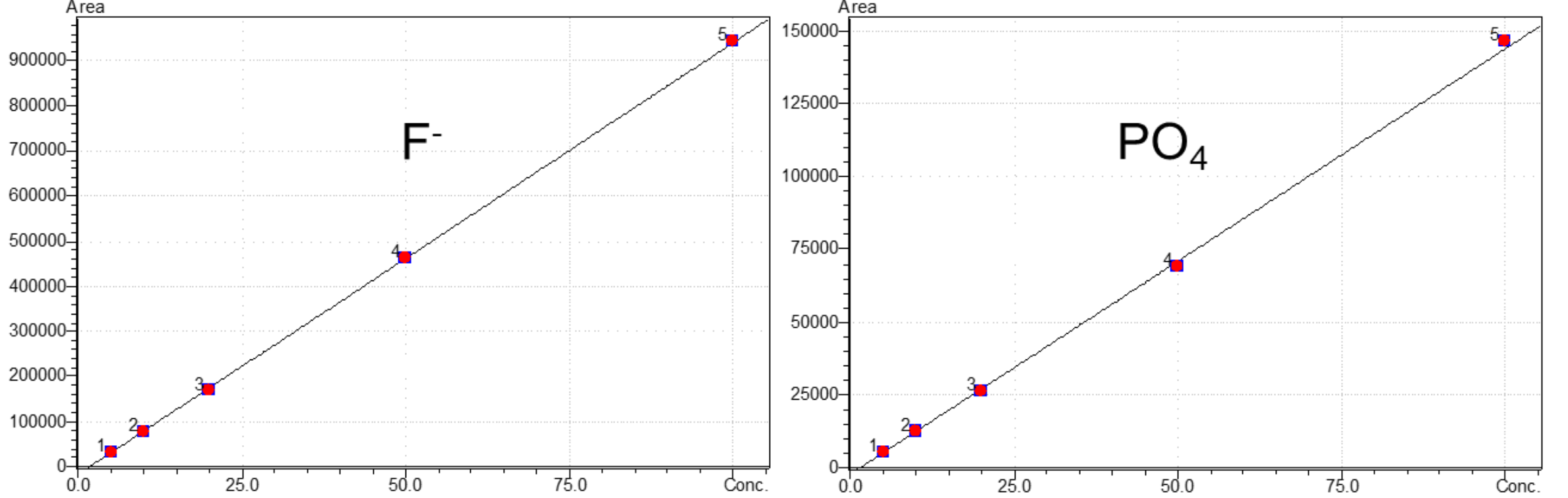


Figure 3: Calibration curves for fluoride and phosphate used for quantification

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 Table 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 1 mol/L LiPF₆ contains approximately 16 g/kg fluoride.

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.

4. 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 technology is suitable to support the optimization process for the recycling procedures.