



Recycling of low value components using high purity pre-treatment, direct recycling and green hydrometallurgical approaches for recycling of Lithium Ion and Sodium Ion batteries.

D4.1 Wastewater chemistry determined

WP4 – Water remediation and lithium extraction

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LIST OF ABBREVIATIONS

CD	conductivity detector
DEC	diethyl carbonate
DMC	dimethyl carbonate
EC	ethylene carbonate
EMS	ethyl methyl carbonate
FID	flame ionization detector
GC	gas chromatography
HR	high resolution
IC	ion chromatography
InC	inorganic carbon
ICP-OES	inductively coupled plasma – optical emission spectroscopy
IEC	ion exclusion chromatography
LOD	limit of detection
MS	mass spectrometry
PC	propylene carbonate
SPE	solid phase extraction
TC	total carbon
TDS	total dissolved solids
TOC	total organic carbon

1. Executive Summary

A workflow for the characterization of the process water was established and applied on different samples from the project consortium. In order to analyse the water chemistry, the categories were defined: elemental composition, conducting salt and the volatile compounds. In all three categories, the analytes were determined with the chosen methodology and the water chemistry could be successfully determined.

2. Introduction

Physicochemical characterization of wastewater as feeds in water remediation and lithium extraction processes will be done. The characterization shall include metal concentration, COD, BOD, ammonia, phosphate and volatiles components among others. This deliverable will be a result of Task 4.1.

3. Determination of the water chemistry

3.1 General analysis pathway

To obtain the needed information about the composition of the process water, several methods need to be applied. In Figure 1, the general scheme of the analysis pathway is shown. The elemental composition like the metals, fluorine or chlorine were assessed by ICP-OES and ion chromatography, respectively. The conducting salt and other ionic compounds like hydrolysis or decomposition products were determined by ion (exclusion) chromatography. Here, the possibility between the hyphenation with mass spectrometry for identification and standard detection with a conductivity detector for quantification is possible. For the volatile organic compounds, deriving from the solvents of the electrolyte, gas chromatography was chosen. Similar to the analysis of the conducting salt, here different detectors were applied for identification and quantification respectively.

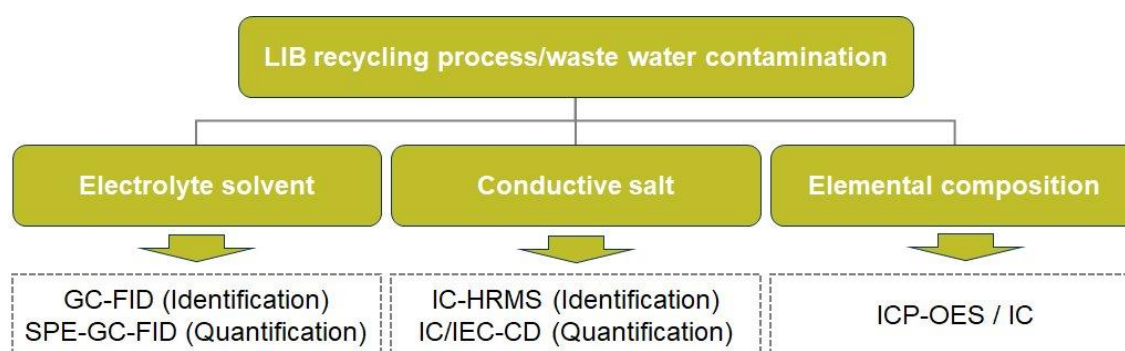


Figure 1. Schematic diagram for the characterization pathway of the process water.

3.2 Samples

Several process water samples from the work package partners were investigated.

3.3 Analysis and determination of the composition

Determination of the elemental composition

Besides the elemental composition of the process water, additional parameters like the pH value and other parameters were determined during the analysis. In Table 1 an overview about the determined parameters is given.

Table 1. Exemplary physicochemical parameters which were obtained from the process water samples.

Parameter	TOC	IC*	TC	TDS	Conductivity
UNIT	mg/L	mg/L	mg/L	mg/L	mS/cm

The elemental composition was - determined by ICP-OES. Here, above all, the metals were quantified. Typically, concentration values were in the range of 0.0009-4 mg/L for elements like cobalt, copper, nickel, zinc, iron, aluminium or manganese. Alkali and Earth alkali elements (Na, Ca, Mg, K > 45 mg/L) were determined as well, however in higher ranges, especially for lithium (333 mg/L). Si (2.7 mg/L) and B (1.1 mg/L) as non-metals were target elements for the ICP-OES as well. On the other hand, anions like halides and inorganic salts besides the conducting salt were determined by ion chromatography. This included fluoride (40.4 mg/L), chloride (38.5 mg/L) and bromide (>LOD) as well as nitride (>LOD), sulphate (167.5 mg/L) and phosphate (6.2 mg/L).

Investigation of the conducting salt and corresponding components

In Figure 2 a typical chromatogram during the analysis of the process water is shown.

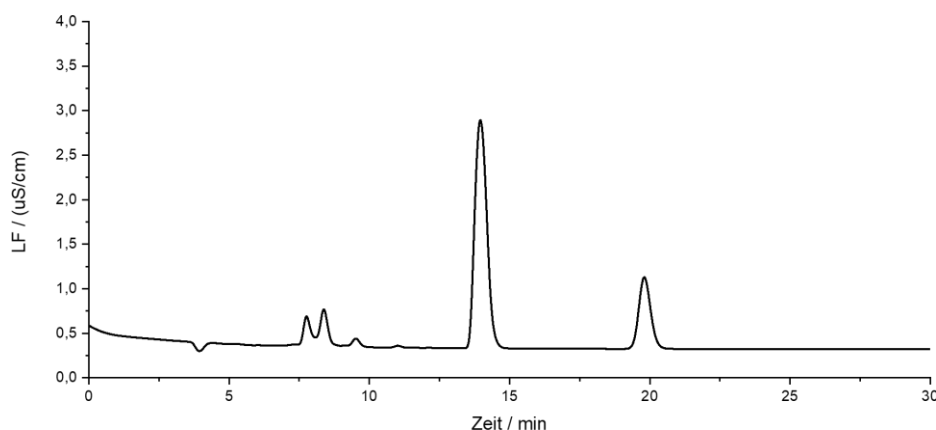


Figure 2. Ion chromatogram of process water which displays typical anions like fluorine, chlorine or PF₆.

The determined anions in the process water were fluoride and mainly hexafluorophosphate in different concentration ranges up to 16100 mg/L. Besides these main compounds also hydrolysis products like difluorophosphate or organo(fluoro)phosphates were found but not quantified due to the lack of commercially available standards.

Analysis of the volatile compounds

Figure 3 shows a GC-FID measurements for the quantitative assessment of the linear and cyclic carbonates. For identification (SMPE)-GC-MS was applied in order to evaluate also low concentrated compounds like aging products and additives.

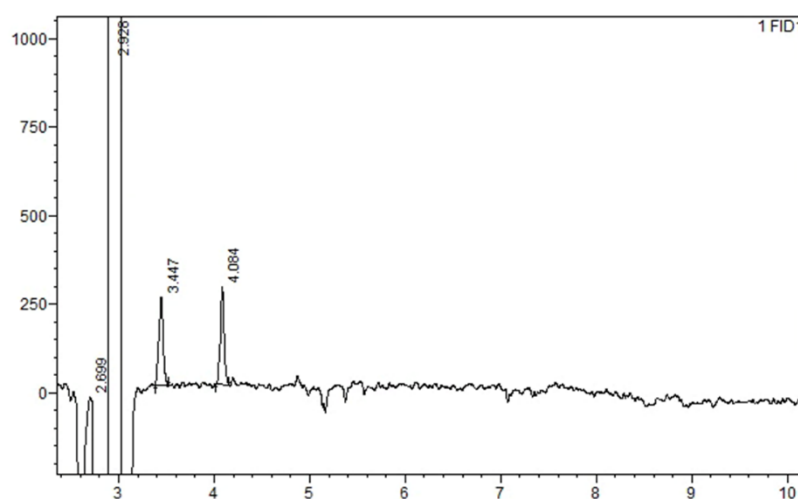


Figure 3. GC chromatogram of a process displaying linear and cyclic carbonates.

Figure 3 shows a GC-FID measurements for the quantitative assessment of the linear and cyclic carbonates. For identification (SMPE)-GC-MS was applied in order to evaluate also low concentrated compounds like aging products and additives. An overview is shown in Table 2.

Table 2. Overview of the determined volatile compounds.

Compound	mg/L
DMC	>4500
EMC	>35600
DEC	>27200
PC	>6600
Fluorobenzol	Identified
Butyl-methyl-carbonate	Identified

4. Conclusions

The overall assessment of the composition of the process water was successful. With the combination of the different methods, it was possible to determine the composition. Furthermore, while not all typical compounds were found, the methods are able to investigate these as well. So, for further samples from the processes, the composition can be determined even if the feedstock of cells is varied. Additionally, process water samples after distillation can be analysed to see changes in the composition and the efficiency of the clean-up step.