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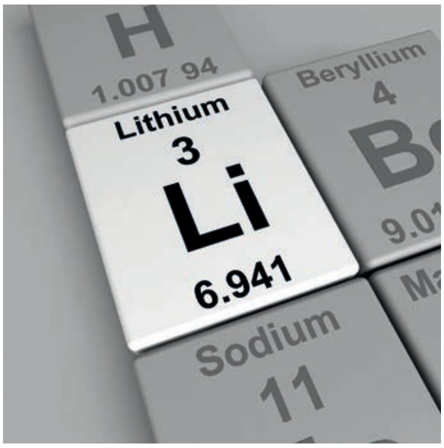

TACKLING SAMPLE PREPARATION FOR ELEMENTAL ANALYSIS IN THE **LITHIUM-ION BATTERY INDUSTRY**

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Tackling Sample Preparation for Elemental Analysis in the Lithium-Ion Battery Industry

1.

Abstract

Over the last years, there has been a growing awareness to stop global warming and to keep our planet healthy. It is clear that we need changes in our way of life and in our technology. We need ideas to use energy in a better way. A clear step is the move from combustion engines to electric vehicles.

Batteries are evolving and Li-ion battery is the chosen technology so far. Consequently, we must understand how to improve batteries performance, and the chemical analysis of their components is a necessary step.

Materials for anodes, cathodes and electrolytes should be fully characterized.

In this eBook, we explain how microwave-assisted digestion has become an essential ally for sample preparation of battery materials before measurements by inductively coupled plasma optical emission spectrometry. After a brief introduction to fundamentals, several procedures are presented for analysis of anode, cathode, and electrolyte materials. We are going to demonstrate how the use of microwave-assisted closed vessel digestions makes feasible the metal analysis of several components used in the Li-ion battery industry. Moreover, this approach led to shorter digestion cycles, using lower volumes of reagents and higher temperatures without compromising safety aspects.

The implementation of Li-ion battery technology aims to a more sustainable world, so a green approach should be taken to address this new analytical challenge. The developed procedures are fully compatible with green technologies and incorporate green chemistry attributes to improve our environment. This eBook is a practical step toward easy-to-use sample preparation procedures for accurate analysis of Li-ion batteries components. In other words, better chemistry through microwave technology supporting a better world with green technologies.

Hope you enjoy the ride. Welcome!

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2.

Energy transition driven by Li-ion battery

Humans and animals need food. Plants need sun and chemical nutrients. Devices need batteries. We all need energy. Energy comes from various sources and they all must be sustainable. Currently, combustion engines in vehicles are still powered by fossil fuels and, despite being a successful technology for decades, they must be changed for cleaner alternatives. In this context, vehicles powered by batteries have become a major trend towards sustainability.

Electric power revolution is in progress and Li-ion batteries, one of the most advanced rechargeable devices, are the milestone for this new energy transition. They are currently the dominant mobile power sources for portable electronic devices, exclusively used in cell phones and laptop computers, and the preferential powerhouse choice for electric vehicles. Furthermore, Li-ion batteries will be employed also to buffer the intermittent and fluctuating green energy supply from renewable resources, such as sun and wind, to smooth the difference between energy supply and demand. For example, extra solar energy generated during the daytime can be stored in Li-ion batteries that will supply energy at night when sunlight is not available. This approach, if deeply adopted, will result in a dramatic reduction of carbon emission moderating the strong impact our society has on climate change, moving to a more sustainable and green civilization.

Back in the 1990s, the commercialization of Li-ion battery started as the result of intensive research and contributions by many scientists and engineers. Over the last two decades we have seen a continuous “raising the bar” for battery efficiency, the economical driving force for further developments.

Looking at our daily life, we can easily observe that the increasing functionality of mobile electronics continuously demands for better Li-ion batteries. For example, the trends in new smartphones are to charge the batteries less frequently, more rapidly and to reduce size and weight of batteries.

Nowadays, renewable resources, electric and hybrid vehicles require batteries with not only high power, high capacity, high charging rate and long life, but also dramatically improved safety performance and low cost. An additional challenge to the development roadmap came from two of the main commodities driving this revolution: lithium and cobalt. Historically, demand for Li and Co was driven by multiple end sectors, although battery industry quickly boosts it. Raw material availability is limited, especially for Co, and new developments have to take care of the sustainability of the mining processes. As a result, the price for these two commodities spikes and many battery producers work to reduce the overall material needed per kWh, additionally they focus on less cobalt-intensive chemistries as well as improving the recycling technologies.

To meet all these needs, intensified research is required to develop next generation Li-ion batteries with dramatically improved performances, including improved specific energy and volumetric energy density, cyclability, charging rate, stability and safety. This process requires the most advanced characterization techniques to enable research teams to optimize and further evolve the current battery energy storage to a real asset for a more sustainable and green society.

But, what is a battery?

3.

Lithium-ion Batteries main components and their analysis: the importance of elemental determination

Battery is an electrochemical device to store energy and all batteries are composed of two electrodes connected by an electrolyte. According to Armand and Tarascon [1] "when these electrodes are connected by means of an external device, electrons spontaneously flow from the more negative to the more positive potential. Ions are transported through the electrolyte, maintaining the charge balance, and electrical energy can be taped by the external circuit. In secondary, or rechargeable, batteries, a larger voltage applied in the opposite direction can cause the battery to recharge". Nowadays, Li-ion batteries are the choice to power portable electronics and hybrid/full electric vehicles. Nitta et al. stated that "Li-ion batteries have an unmatchable combination of high energy and power density". These authors also listed fundamental advantages of Li-ion batteries: Li has the lowest reduction potential of any element and, consequently, Li-based batteries have the highest possible cell potential [2]. They also highlighted that Li is the third lightest element and has one of the smallest ionic radii of any single charged ion. These factors are related to the high power density of Li-ion batteries. Yoshino has described Li-ion battery as a "non-aqueous secondary battery using transition-metal oxides containing Li ion such as $LiCoO_2$ as a positive electrode and carbonaceous materials as a negative electrode" [3]. Processes of charge or discharge of Li-ion battery are based on electrochemical processes involving Li ions between these electrodes. Li-ion battery is composed by two electrodes, anode and cathode, and a polyolefin-based separator soaked with an electrolyte. According to Nowak and Winter [4] the electrolyte consists of a conducting salt, e.g. lithium tetraborate, lithium bis-(oxalato) borate, or lithium hexafluorophosphate, dissolved in a mixture of different linear carbonates, e.g. dimethyl carbonate. Anode materials, i.e. the negative electrode, should allow entrance and exit of Li ions. These materials can be divided in three groups [4]: (1) intercalation/de-intercalation materials (carbon based materials and $Li4Ti5O_{12}$);

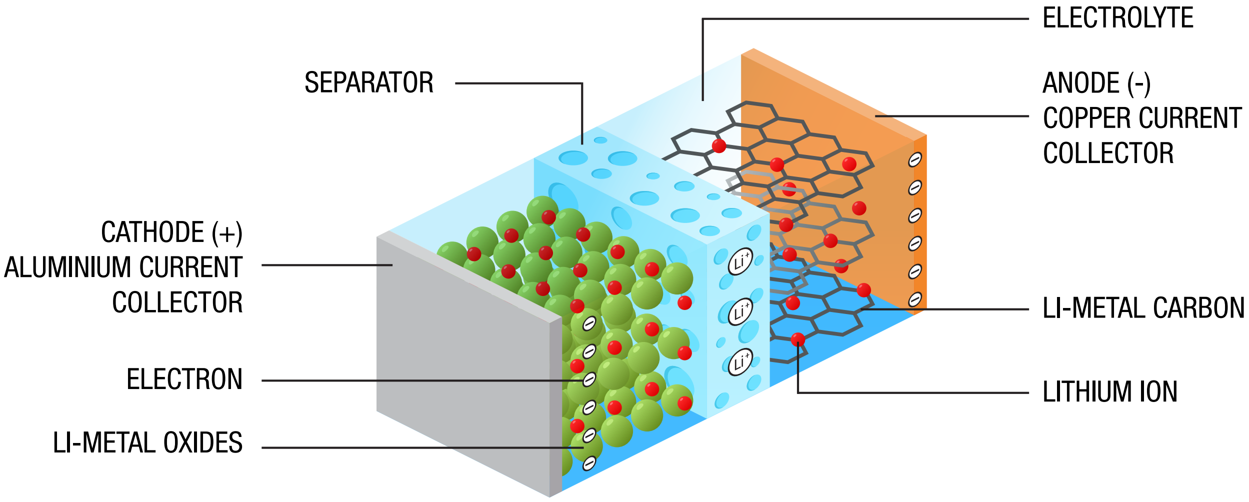

Diagram of a Lithium-Ion Battery

(2) alloy/de-alloy materials (e.g. Si, Ge, Bi and Sn); and (3) metal oxides. Graphite-containing anodes are the reference for commercial Li-ion batteries. The positive electrode, i.e. the cathode, is generally composed by lithium-containing oxides, such as lithium cobalt oxide, lithium manganese oxide, and ternary combination of nickel, cobalt, manganese and lithium, and lithium iron phosphate.

The performance of anode and cathode materials affects Li-ion batteries energy density, safety, and lifespan. One important aspect about the performance and lifecycle of these materials is related to their composition and formed decomposition products along their lifetime. It is important to know the chemical composition of all components of batteries to better understand aging effects and expand their lifecycle. Consequently, chemical analysis is a must for determining stoichiometries of the active materials, their changes along charge/discharge cycles and impurities.

Nowadays, elemental analysis is frequently based on plasma methods. Inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS) are used depending on the required sensitivity. However, despite instrumental alternatives for direct solid analysis, both instrumental methods generally involve analysis of solutions introduced by pneumatic nebulization. It means that solid samples, i.e. anode, cathode and separator materials of batteries, should be converted in representative solutions before instrumental analysis. The sample preparation step exerts a pronounced effect on the quality of analytical results and inorganic materials used as electrodes in Li-ion batteries are hardly decomposed.

Mixed oxides and carbon-containing materials are resistant to chemical attack and special procedures should be developed for efficient conversion of these materials in representative solutions. To break apart chemical bonds that keep these elements together we must apply appropriate reagents and high temperature. However, to be compatible with a green technology we must develop green digestion procedures. Ideally, we should not use or we should try to significantly reduce the use of critical reagents, such as hydrofluoric acid, perchloric acid and even high volumes of concentrated acids, and we should use a clean form of energy to heat solutions and, consequently, to promote chemical reactions.

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DIGESTION

Nowak and Winter [4] emphasized that considering the huge volume of publications it is astonishing that the research field of elemental analysis of batteries is in a so-early stage. They also stated that: "…it is clear already today, that the continuous improvement and adaptation of advanced analysis methods will be the key for the accurate chemical analysis of batteries and its components, thus unraveling the unanswered degradation mechanisms and those to come.".

This eBook collects the efforts of Milestone Application Team around the world to address the emerging analytical need of state-of-the-art procedures for sample preparation of main components of batteries.

As it will be discussed in Section 6, microwave-assisted digestion methods are applicable and less aggressive reagents can be used at high temperatures in closed vessels. Adopting this technology, green digestion procedures can be developed for sample preparation and these are fully compatible with the advent of a greener technology for powering devices and vehicles.

4.

Addressing sample preparation of Lithium-Ion Batteries components with microwave chemistry

Some chemical reactions occur spontaneously. Others depend on a source of energy to start and to convert reagents to products. These chemical processes are promoted by providing energy and their speed depends on the temperature. Typically, sample preparation, i.e. the conversion of solid samples in representative solutions, is sped up by increasing the temperature of the reaction medium. During many centuries heating was provided by using flames, heating plates, and water, oil, or sand baths. All these devices operate by heating the outer vessel wall containing samples and reagents and then transferring the heating to the reaction medium. Of course, part of the heating energy is lost to the environment.
We need something more efficient and we have it. Microwave radiation has attractive advantages for heating solutions containing ions and dipoles. The energy of microwaves interacts directly with these charged species and increases their kinetic energy. This kinetic energy is converted in heating and the temperature of solution rapidly increases. These processes allow a better use of applied power without waste of energy. As we know from our lives in this amazing planet, energy is a key issue and it must be well used.
This technology was developed by Milestone since late 80's and it is fully accepted and implemented in laboratories for sample preparation, extraction procedures, synthesis of chemical compounds and new materials. In the sample preparation field, this technology promoted the development of closed reactions vessels using new polymers and sensors for real-time measurements of temperature and pressure. Nowadays, we have the instruments to follow chemical processes and apply the right amount of energy to control them. It should be stressed that microwave radiation not only promotes fast heating of solutions, but also brings the possibility to develop new chemical processes

as demonstrated for organic samples [5].
But, how does microwave radiation improve sample preparation for inorganic samples?
How does microwave radiation improve sample preparation for typical samples related to Li-ion batteries?
There are two general approaches to tackle these questions. Firstly, we may consider that we do not need to completely transfer all the components of solid samples to solution phase. We just need to transfer to solution those components that we need to determine. Recently, this strategy was tested for several inorganic samples and it was demonstrated that even less concentrated solutions of nitric acid (2 or 4 mol/L) were effective to bring elements to solution. Therefore, the use of nitric acid diluted solutions as an alternative to HF is a feasible procedure for quantitative analysis of zinc oxide, kaolin, zinc residue, and zinc sulfide [6].
The second strategy is based on the use of microwave reactors designed to support high temperatures (e.g. 280 °C), high pressures (e.g. 199 bar) and aggressive chemical medium.
At this point it is nice to remember that the development of new experimental procedures relies either on new ideas or on new devices. If we have vessels that allow working at critical reaction conditions without compromising safety, we can develop procedures at high temperatures (a key parameter!) even without using high volumes of concentrated reagents. This was the strategy adopted for developing the procedures described in Section 6 for sample preparation of Li-ion battery components. By adopting this approach we are moving towards the development of green digestion procedures.
As you may see by consulting Section 6, procedures were developed using two modern microwave instruments: ETHOS UP and ultraWAVE. All procedures used small volumes of aqua regia and other reagents - such as sulfuric and phosphoric acids - were used for samples more resistant to chemical attack. Maximum temperatures varied from 230 to 280 °C and heating program was set in two steps, i.e. time to

ETHOS UP - Advanced Microwave Digestion System for Elemental Analysis

ultraWAVE - Single Reaction Chamber Microwave Digestion System for Elemental Analysis reach the target temperature and time remained at the target temperature. Despite using aggressive chemical reagents, three points should be highlighted: (1) volumes of these reagents were significantly reduced if we compare them with the volumes used in the conventional procedures without using microwave radiation and special designed reactions vessels; (2) heating times were shorter compared to those typically adopted when using open vessels conductively heated; and (3) components of Li-ion batteries, such as alloys, oxides, and graphite, are resistant to chemical attack.

Generally, sample digestion of organic samples, such as plant and animal tissues, are easily performed using nitric acid plus hydrogen peroxide in closed vessels at temperatures around 180 – 220 °C. However, digestion conditions are more stringent for inorganic samples. Typically, these materials involve chemical bonds among their components that are harder to break and the use of more aggressive reagents and mixtures of reagents are required. Temperature also exerts a critical influence and particle size effects are observed.

One interesting example is presented in Section 6 related to graphite and graphene nanotubes. Graphite samples require a mixture composed by sulfuric and perchloric acids and vanadium was used as a catalyst to break C-C bonds. Efficient digestions were reached at 240 and 280 °C when using ETHOS UP and ultraWAVE, respectively. On the other hand, vanadium was not needed when digesting graphene nanotubes using ultraWAVE at a maximum temperature of 270 °C. Sample masses and volume of reagents could be also compared. Please, check respective procedures on Section 6.

As a rule of thumb, we may generalize that digestion of inorganic samples depends critically on the choice of reagents and the maximum temperature applied for promoting reaction conditions which provide enough energy to break stable chemical bonds among sample constituents.

NOTE: If perchloric acid is recommended for special applications, all safety conditions must be strictly followed and, when possible, it should be avoided.

5.

Greener sample preparation for greener energy transition

As discussed in previous chapters, microwave radiation brought a new dimension for developing better accuracy for sample digestion. In the old times, chemists played with concentrated reagents and temperatures to convert solid samples in representative solutions. Vessels designed for performing chemical processes were simple. Frequently, open vessels were used but despite some advantages, such as low cost and availability, the applied temperatures were limited by the used reagents and procedures were affected by losses caused by volatilization and contamination. Some closed vessels were available, but they had no built-in sensors for measuring the developed pressure and temperature during chemical processes and safety was a critical issue. In this scenario, analysts had to use high volumes of concentrated reagents to perform digestions when using open vessels. Concentrated sulfuric acid was required when higher temperatures were needed for promoting chemical processes. Concentrated perchloric acid was generally used for samples containing organic compounds. Despite effective, analytical errors may affect inorganic analysis owing to losses and contamination. Of course, these procedures cannot be considered as compatible with green chemistry principles [5] considering the volumes of concentrated reagents, volumes of generated residues, and wasted energy.

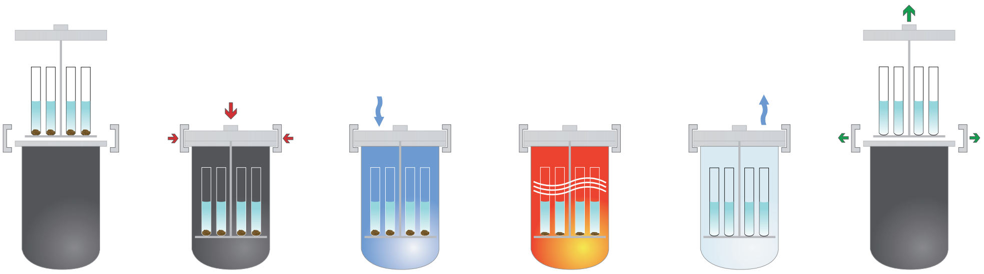
Clearly, sample preparation strategies required advances for making this critical analytical step compatible with modern instrumental analysis. As previously mentioned, advancements could come from new ideas that bring new devices. The combination of both could fertilize this area and analysts could propose improved procedures for modernizing the conversion of solid samples in representative solutions using simple reagents. One major step forward was the advent of microwave radiation for sample preparation.

We already know that microwave radiation can rapidly heat solutions containing ions and dipoles. However, we may say that this is only one of the advantages compared to conventional conductive heating. Another important point is that digestion vessels specially designed for microwave ovens are built with materials transparent to microwave radiation and the energy associated with this radiation is directly absorbed by solutions containing ions and dipoles. On the other hand, microwave radiation is not appreciably absorbed by the gas phase in a closed vessel and, consequently, a gradient of temperature results between liquid and gas phases. This gradient of temperature promotes condensation processes and it was demonstrated that nitric acid can be regenerated during digestion if air or oxygen is

present inside the vessel [7]. Details about these processes are beyond our goals here, but literature is broadly available [8-9]. As demonstrated, efficient digestions of animal and plant tissues can be promoted using concentrations as low as 0.7 mol/L nitric acid plus a small volume of hydrogen peroxide [10].

Implicit in the previous discussion is the information that the use of microwave radiation led to the development of new digestion vessels that could support high pressure, high temperature and aggressive reagents. Additionally, this technology also brought the development of temperature and pressure sensors that follow the evolution of digestion processes in real time. Consequently, analysts can better understand how chemical reactions proceed along heating and how much energy is needed for promoting digestion processes.

The evolution of this technology has led to the development of the single reaction chamber concept, SRC [11]. This instrument is also based on microwave heating and a rack containing all sample vessels is inserted into the SRC containing a volume of water to partial immersion of these vessels. This chamber is hermetically closed and pressurized with an inert gas. The vessels inside the SRC can reach temperatures as high as 280 °C and pressures as high as 199 bar. As an additional advantage and owing to the characteristics of the SRC concept, these extreme conditions of pressure and temperature can be reached using simple vessels and different racks.



SRC Operating Sequence

One important consequence of this type of technology is that the possibility of reaching really high temperatures can be used to promote digestions of refractory samples without requiring high volumes or concentrations of acids. In other words, green chemistry procedures can be implemented using SRC technology.

What do we mean when we talk about green chemistry procedures for sample preparation? We have discussed green chemistry features in a previous book [5] and a series of attributes were proposed:

1. Production of reagents: raw material, energy, time, purity, sub products, yield, and generated waste.
2. Chemical and physical properties of reagents: boiling point, flammability, corrosiveness, stability, shelf life, ease of recovery, and ease of handling.
3. Lifetime of equipment, vessels and sensors.
4. Sample amount needed.
5. Mass, volume and concentration of reagents.
6. Need of gases or special reagents.
7. Energy needed for promoting and keeping the reaction system heated – use of energy-effective apparatus.
8. Reaction conditions: temperature, pressure and time.
9. Generation of too reactive or dangerous products.
10. Volume and toxicity of gases generated.
11. Risk to the analyst and to the environment.
12. Volume of generated residues.
13. Recycle of reagents.

The implementation of SRC concept in a microwave instrument allows implementing several of these attributes. For instance, volume and concentrations of reagents can be decreased, only nitrogen or argon is needed to pressurize the chamber, microwave energy is efficiently absorbed by the solution inserted in the chamber, reaction conditions (i.e. temperature, pressure, and time) are controlled, gases generated are kept inside the chamber before releasing and risks to the analyst and to the environment are minimized, volume of generated acid residues is decreased, and reagents can be recycled using a specially developed procedure [12].

We may conclude that microwave radiation associated with SRC technology represents to sample preparation area a leap forward towards green chemistry procedures. If our cars are becoming greener, our labs also should follow this direction. All steps towards sustainability are important. As we recommended before, Think Green, Act Green! [5].

6.

Guidelines for sample preparation and analysis of Lithium-Ion Battery components

Lithium sources

Cathode materials

Anode materials

Electrolyte

Recycling material

6.1 **Instrumentation**

Microwave-assisted Acid Digestion
Sample acid digestion was performed with two types of system based on different microwave technologies.

The **ETHOS UP** is a flexible and high performing platform used for elemental analysis. Equipped with easyTEMP contactless sensor, it directly controls the temperature of all samples and solutions, providing accurate temperature feedback to ensure complete digestion in all vessels and high safety. ETHOS UP works with SK-15 rotor capable of high temperature (up to 300 °C) and pressure (up to 100 bar). The SK-15 also features Milestone's patented "vent-and-reseal" technology for controlling the internal pressure of each vessel. This ensures complete, safe and reproducible digestions of even the most difficult samples.

Milestone ETHOS UP

The **ultraWAVE**, developed and patented by Milestone, with Single Reaction Chamber (SRC) technology utilizes high-performance stainless steel, allowing to reach higher pressures and temperatures (up to 199 bar and 300°C respectively) and to use any type of acids. Disposable vessels eliminate the need to assemble, disassemble or clean between processing. Just as important, dissimilar samples can be processed simultaneously using any mixture of disposable glass, quartz or TFM vials, thus saving time and money. The ultraWAVE is simply the fastest, easiest and most efficient digestion system ever made.

Milestone ultraWAVE

Determination of Metals
The instrument used for metals and trace metals determination was an inductively-coupled plasma optical emission spectrometer (ICP OES), with axial view and equipped with automatic sampler.

6.2 **Operating sequence**

ETHOS UP operating sequence

1. Sample is weighed into the TFM vessel.
2. According to each different sample matrix, suitable reagent mixture (refer to single material chapters) is added to the vessel.
3. The reagent mixture is properly mixed with the sample.
4. Vessels are closed with TFM covers and introduced into the rotor body.
5. The suitable microwave program is set to the software and started (refer to single material chapters).
6. Vessels are cooled down properly inside the microwave cavity and then opened.
7. The resulting solutions are transferred into 50 mL volumetric flasks. Vessels are then rinsed twice with distilled water and rinsates are collected into the same flask.
8. Solutions are brought to volume with distilled water.

ultraWAVE operating sequence

1. TFM single reactor vessel is loaded with 130 mL of DI water and 5 mL of nitric acid (HNO_3, 65%).
2. Samples are weighed into ultraWAVE vials.
3. According to each different sample matrix, suitable reagent mixture (refer to single material chapters) is added to the vial and properly mixed (5 position rack vials are suggested for these applications).
4. Vials are capped with plug-in TFM covers and placed into the rack. The rack is properly positioned into ultraWAVE system.
5. The heating program is set to the software and started (refer to single material chapters). The reactor chamber is then automatically closed, inert gas (N_2) is pre-loaded into the reactor and the microwave program starts.
6. Once cooled, the remaining pressure is automatically released from the reactor and the system automatically stops. The chamber can be opened and the sample rack removed.
7. The resulting solutions are transferred into 50 mL volumetric flasks. Vials are then rinsed twice with distilled water and rinsates are collected into the same flask.
8. Solutions are brought to volume with distilled water.

ICP OES Instrumental Parameters

The instrument setup and the operating conditions are reported in the following table:

Parameter	Setting
RF applied power (kW)	1.3
Plasma gas flow rate (L/min)	15
Auxiliary gas flow rate (L/min)	1.5
Nebulizer gas flow rate (L/min)	0.75
Replicate read time (s)	5
Stabilization delay (s)	30
Sample uptake delay (s)	30
Pump rate (rpm)	15
Rinse time (s)	15
Replicates	3
Emission lines (nm)	Indicated in each table of data

6.3 **Reagents**

a. HNO_3, nitric acid, 65%, ACS reagent (Sigma-Aldrich)
b. HCl, hydrochloric acid, 37%, ACS reagent (Sigma-Aldrich)
c. HF, hydrofluoric acid, 48%, ACS reagent (Sigma-Aldrich)
d. H_3PO_4, orto-phosphoric acid, 85%, ACS reagent (Sigma-Aldrich)
e. H_2SO_4, sulphuric acid, 96-98%, ACS reagent (Sigma-Aldrich)
f. $HClO_4$, perchloric acid, 70%, ACS reagent, technical grade (Sigma-Aldrich)
g. Vanadium (V) standard solution, 1000 mg/L V in nitric acid (TraceCERT, Sigma-Aldrich)
h. Periodic table mix 1 for ICP, 10 mg/L (TraceCERT, Sigma-Aldrich): Al, As, Ba, Be, Bi, B, Ca, Cd, Cs, Cr, Co, Cu, Ga, In, Fe, Pb, Li, Mg, Mn, Ni, P, K, Rb, Se, Si, Ag, Na, Sr, S, Te, Tl, V and Zn in 10% V/V nitric acid (contains HF traces)
i. Periodic table mix 2 for ICP, 10 mg/L (TraceCERT, Sigma-Aldrich): Au, Ge, Hf, Ir, Mo, Nb, Pd, Pt, Re, Rh, Ru, Sb, Sn, Ta, Ti, W, and Zr in 5%V/V hydrochloric acid and 1% V/V hydrofluoric acid (contains HNO_3 traces)
j. Yttrium standard for ICP, 10000 mg/L (TraceCERT, Sigma-Aldrich)

6.4 **Methods**

LITHIUM SOURCES

6.4.1 **Lithium Ores: Spodumene**

Spodumene is a pyroxene mineral consisting of lithium aluminum inosilicate ($LiAlSi_2O_6$). It is the most widely exploited mineral source of lithium (theoretical lithium content = 3.73%). Other lithium-bearing pegmatite silicates include lepidolite and petalite. Although in the past industry transitioned to extracting lithium from brines, nowadays the exploding demand for lithium has made the exploration for and development of spodumene deposits a highly attractive endeavor.

■ Method for **ETHOS UP**

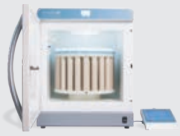
SAMPLE MASS
100 mg

FINAL VOLUME
50 mL

REAGENTS
3 mL of H_3PO_4, 3 mL of H_2SO_4 and 2 mL of HF (dil 1:3)

MICROWAVE HEATING PROGRAM

	Time	*Temp*	*Power*
1	25 min	230°C	1800 W
2	30 min	230°C	1800 W



■ Method for **ultraWAVE**

SAMPLE MASS
100 mg

FINAL VOLUME
50 mL

REAGENTS
1.5 mL of H_3PO_4, 1.5 mL of H_2SO_4 and 2 mL of HF (dil 1:3)

MICROWAVE HEATING PROGRAM

	Time	*T1*	*T2*	*Power*	*P*
1	15 min	280°C	60°C	1500 W	40 bar
2	20 min	280°C	60°C	1500 W	40 bar

■ Method **Results**

Note: ETHOS UP and UW led to efficient digestions and results using ICP OES did not present any statistical difference. Consequently, we have decided not to specify for each set of results the used system because both led to accurate data.

Major elements in Spodumene sample

	Determined concentration	*RSD (n = 6)*
Al 396.152	12.9 %	1.67 %
Li 670.783	2.95 %	0.92 %
Si 251.611	27.9 %	1.12 %

LITHIUM SOURCES

6.4.2 **Lithium Ores: Lepidolite**

Lepidolite is a phyllosilicate mineral with chemical formula $KLi_2AlSi_3O_{10}(OH,F)_2$. It is the most abundant lithium-bearing mineral (theoretical lithium content = 3.84%) and is a secondary source of this metal. Li extraction processes from lepidolite have been researched actively because of their widespread distribution, the characteristic of being poor in iron, and the additional contents of rare metals, such as rubidium (Rb) and cesium (Cs).

Method for **ETHOS UP**

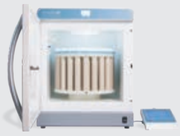
SAMPLE MASS
100 mg

FINAL VOLUME
50 mL

REAGENTS
3 mL of H_3PO_4, 3 mL of H_2SO_4 and 2 mL of HF (dil 1:3)

MICROWAVE HEATING PROGRAM

	Time	*Temp*	*Power*
1	25 min	230°C	1800 W
2	30 min	230°C	1800 W



Method for **ultraWAVE**

SAMPLE MASS
100 mg

FINAL VOLUME
50 mL

REAGENTS
1.5 mL of H_3PO_4, 1.5 mL of H_2SO_4 and 2 mL of HF (dil 1:3)

MICROWAVE HEATING PROGRAM

	Time	*T1*	*T2*	*Power*	*P*
1	15 min	280°C	60°C	1500 W	40 bar
2	20 min	280°C	60°C	1500 W	40 bar

Method **Results**

Note: ETHOS UP and UW led to efficient digestions and results using ICP OES did not present any statistical difference. Consequently, we have decided not to specify for each set of results the used system because both led to accurate data.

Major elements in Lepidolite sample

	Determined concentration	*RSD (n = 6)*
Al 396.152	16.7 %	1.47 %
K 766.491	8.24 %	2.84 %
Li 670.783	1.29 %	3.76 %
Si 251.611	26.3 %	1.31 %

LITHIUM SOURCES

6.4.3 **Lithium Ores: Petalite**

Petalite, also known as castorite, is a lithium aluminum phyllosilicate mineral $LiAlSi_4O_{10}$. It is an important mineral source of lithium (theoretical lithium content = 2.27%). Upon heating (ca. 500 °C) and applying pressure, petalite converts to ß-spodumene-quartz in the solid solution phase. Petalite, and secondary spodumene formed from it, is generally lower in impurities compared to primary spodumene.

Method for **ETHOS UP**

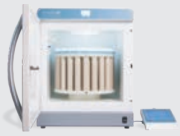
SAMPLE MASS
100 mg

FINAL VOLUME
50 mL

REAGENTS
3 mL of H_3PO_4, 3 mL of H_2SO_4 and 2 mL of HF (dil 1:3)

MICROWAVE HEATING PROGRAM

	Time	*Temp*	*Power*
1	25 min	230°C	1800 W
2	30 min	230°C	1800 W



Method for **ultraWAVE**

SAMPLE MASS
100 mg

FINAL VOLUME
50 mL

REAGENTS
1.5 mL of H_3PO_4, 1.5 mL of H_2SO_4 and 2 mL of HF (dil 1:3)

MICROWAVE HEATING PROGRAM

	Time	*T1*	*T2*	*Power*	*P*
1	15 min	280°C	60°C	1500 W	40 bar
2	20 min	280°C	60°C	1500 W	40 bar

Method **Results**

Note: ETHOS UP and UW led to efficient digestions and results using ICP OES did not present any statistical difference. Consequently, we have decided not to specify for each set of results the used system because both led to accurate data.

Major elements in Petalite sample

	Determined concentration	*RSD (n = 6)*
Al 396.152	16.4 %	0.90 %
Li 670.783	3.46 %	0.70 %
Si 251.611	34.3 %	0.84 %

LITHIUM SOURCES

6.4.4 **Lithium Salts: Lithium carbonate - Li_2CO_3**

Lithium carbonate is a lithium compound which is mainly produced by extracting it from underground brine pools, using precipitation, extraction of other undesired compounds, and addition of sodium carbonate. Up until very recently lithium carbonate has been the focus of many producers of EV batteries, because existing battery designs called for cathodes using this raw material.

Method for **ETHOS UP**

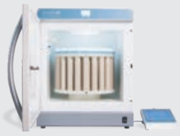
SAMPLE MASS
1000 mg

FINAL VOLUME
50 mL

REAGENTS
5 mL of HNO_3

MICROWAVE HEATING PROGRAM

	Time	*Temp*	*Power*
1	15 min	180°C	1800 W
2	10 min	180°C	1800 W



Method for **ultraWAVE**

SAMPLE MASS
1000 mg

FINAL VOLUME
50 mL

REAGENTS
3 mL of HNO_3 + 1 mL H_2O

MICROWAVE HEATING PROGRAM

	Time	*T1*	*T2*	*Power*	*P*
1	5 min	180°C	60°C	1500 W	40 bar
2	10 min	180°C	60°C	1500 W	40 bar

LITHIUM SOURCES

6.4.5 **Lithium Salts: Lithium hydroxide - LiOH**

Lithium hydroxide is a lithium-based compound with a crucial distinctive property compared to lithium carbonate: it decomposes at a lower temperature, allowing the process of producing battery cathodes to be more sustainable and the final product to be long lasting. Additionally, key advantages of lithium hydroxide battery cathodes in relation to other chemical compounds include better power density (more battery capacity), longer life cycle and enhanced safety features.

Method for **ETHOS UP**

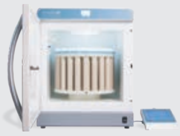
SAMPLE MASS
1000 mg

FINAL VOLUME
50 mL

REAGENTS
5 mL of HNO_3

MICROWAVE HEATING PROGRAM

	Time	*Temp*	*Power*
1	15 min	180°C	1800 W
2	10 min	180°C	1800 W



Method for **ultraWAVE**

SAMPLE MASS
1000 mg

FINAL VOLUME
50 mL

REAGENTS
3 mL of HNO_3 + 1 mL H_2O

MICROWAVE HEATING PROGRAM

	Time	*T1*	*T2*	*Power*	*P*
1	5 min	180°C	60°C	1500 W	40 bar
2	10 min	180°C	60°C	1500 W	40 bar

CATHODE MATERIALS

6.4.6 **LCO – Lithium Cobalt Oxide**

Lithium cobalt oxide ($LiCoO_2$) is one of the most common cathode Li-ions. Its high specific energy makes Li-cobalt the popular choice for mobile phones, laptops and digital cameras. On the other hand, the drawback of Li-cobalt is a relatively short life span, low thermal stability and limited load capabilities (specific power).
The purposes of LCO analysis are 1) to determine the composition of the main elements (QC/Production) and 2) to evaluate the purity of the raw material (QC/R&D).

■ Method for **ETHOS UP**

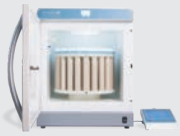
SAMPLE MASS
500 mg

FINAL VOLUME
50 mL

REAGENTS
2 mL of HNO_3 and 6 mL of HCl

MICROWAVE HEATING PROGRAM

	Time	*Temp*	*Power*
1	25 min	230°C	1800 W
2	15 min	230°C	1800 W



■ Method for **ultraWAVE**

SAMPLE MASS
500 mg

FINAL VOLUME
50 mL

REAGENTS
1 mL of HNO_3 + 3 mL of HCl

MICROWAVE HEATING PROGRAM

	Time	*T1*	*T2*	*Power*	*P*
1	15 min	250°C	60°C	1500 W	40 bar
2	20 min	250°C	60°C	1500 W	40 bar

Spike recoveries and Internal standard

Spike standard. Three replicates out of six were spiked with 800 µL of periodic table mix 1 (solution h) and 2 (solution i) for ICP standards respectively, immediately after sample weighing and prior to reagent addition. These worked as recovery studies for elemental impurities.
The concentration of the spiked elements in the final digested solution was 160 µg/L.
Internal standard. 10 µg/mL of Yttrium standard (d) was added to calibration standards, blanks, digested solutions and, where appropriate, to their dilutions (e.g. 500 µL of Y std added to 50 mL of digested solution). This was used as internal standard to correct matrix effects.

■ Method **Results**

Major elements in LCO sample

	Determined concentration	*RSD (n = 3)*
Co 228.615	1.76 %	0.0621 %
Li 610.365	4.34 %	0.761 %

Impurities and spike recoveries in LCO sample

	Determined concentration (µg/L)	*RSD% (n = 3)*	*Spiked determined concentration (µg/L)*	*RSD% (n=3)*	**Spike recovery (%)**
Ag 328.068	7.72	1.10	100	1.41	**116**
As 188.980	<MDL	-	82.0	2.07	**103**
Ba 455.403	11.7	3.03	82.8	4.95	**89**
Be 313.042	<MDL	-	73.2	1.06	**92**
Bi 223.061	103	1.37	180	2.74	**97**
Cd 214.439	<MDL	-	76.2	1.02	**95**
Cr 267.716	19.5	1.82	94.3	0.68	**93**
Cu 324.754	<MDL	-	84.1	0.59	**105**
Fe 234.350	39.6	6.08	113	1.87	**92**
Ir 212.681	<MDL	-	75.0	3.58	**94**
Mn 257.610	26.5	6.66	98.0	1.30	**89**
Mo 202.032	<MDL	-	82.4	2.23	**103**
Na 588.995	299	0.95	371	0.57	**90**
Nb 309.417	<MDL	-	85.9	0.99	**107**
Ni 216.555	99.5	0.14	174	2.85	**93**
Pb 182.143	105	2.69	181	0.78	**95**
Se 196.026	77.9	3.36	151	5.14	**92**
Sn 189.925	21.6	8.50	111	3.83	**111**
Sr 407.771	<MDL	-	82.6	1.03	**103**
Te 214.282	19.3	1.47	109	5.86	**112**
V 292.401	14.07	14.6	88.4	0.80	**93**
Zn 206.200	<MDL	-	87.9	3.86	**110**

The digested solutions were further diluted by 1:2 V/V with water to lower their acid concentration prior to ICP OES analysis. The final spiked concentration was 80 µg/L.

CATHODE MATERIALS

6.4.7 **NMC – Lithium Nickel Manganese Cobalt Oxide**

Lithium Nickel Manganese Cobalt Oxide ($LiNiMnCoO_2$), NMC, has become the go-to cathode powder to develop batteries for power tools, e-bikes and other electric powertrains. It delivers strong overall performance, excellent specific energy, and the lowest self-heating rate of all mainstream cathode powders, which makes it the preferred option for automotive batteries.

The cathode combination is typically one-third nickel, one-third manganese and one-third cobalt, also known as NMC111. Cobalt is expensive and in limited supply. Battery manufacturers are reducing the cobalt content with some compromise in performance. A successful combination is NCM532 with 5 parts nickel, 3 parts cobalt and 2 parts manganese. Other combinations are NMC622 and NMC811. Cobalt stabilizes nickel, a high energy active material.

For this application note NMC532 was used.

The purposes of NMC analysis are 1) to determine the composition of the main elements (QC/Production) and 2) to evaluate the purity of the raw material (QC/R&D).

■ Method for **ETHOS UP**

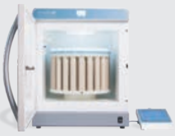
SAMPLE MASS
500 mg

FINAL VOLUME
50 mL

REAGENTS
2 mL of HNO_3 + 6 mL of HCl

MICROWAVE HEATING PROGRAM

	Time	*Temp*	*Power*
1	25 min	230°C	1800 W
2	15 min	230°C	1800 W



■ Method for **ultraWAVE**

SAMPLE MASS
500 mg

FINAL VOLUME
50 mL

REAGENTS
1 mL of HNO_3 + 3 mL of HCl

MICROWAVE HEATING PROGRAM

	Time	*T1*	*T2*	*Power*	*P*
1	15 min	250°C	60°C	1500 W	40 bar
2	20 min	250°C	60°C	1500 W	40 bar

Spike recoveries and Internal standard

Spike standard. Three replicates out of six were spiked with 500 µL of periodic table mix 1 (solution h) and 2 (solution i) for ICP standards respectively, immediately after sample weighing and prior to reagent addition. These worked as recovery studies for elemental impurities.

The concentration of the spiked elements in the final digested solution was 100 µg/L.

Internal standard. 10 µg/mL of Yttrium standard (d) was added to calibration standards, blanks, digested solutions and, where appropriate, to their dilutions (e.g.: 500 µL of Y std added to 50 mL of digested solution). This was used as internal standard to correct matrix effects.

■ Method **Results**

Major elements in NMC532 sample

	Determined concentration	*RSD (n = 6)*
Co 228.615	12.2 %	1.34 %
Li 610.365	7.84 %	6.41 %
Mn 257.610	17.4 %	0.60 %
Ni 231.604	30.3 %	1.22 %

Impurities and spike recoveries in NMC532 sample

	Determined concentration (µg/L)	*RSD% (n = 3)*	*Spiked determined concentration (µg/L)*	*RSD% (n=3)*	**Spike recovery (%)**
Ag 338.289	145	1.44	191	1.60	**93**
As 188.980	121	3.35	178	2.03	**115**
Ba 455.403	<MDL	-	49.9	1.48	**100**
Be 234.861	<MDL	-	45.3	2.11	**91**
Cd 214.439	40.9	8.43	98.4	2.81	**115**
Cu 324.754	<MDL	-	44.8	0.93	**90**
K 766.491	106	2.59	156	0.64	**100**
Mo 202.032	<MDL	-	44.9	5.35	**90**
Pb 220.353	32.5	3.41	80.1	2.88	**95**
Ru 267.876	50.8	6.12	97.6	0.58	**94**
Sn 189.925	<MDL	-	47.1	2.10	**94**
Sr 407.771	5.72	2.14	50.5	2.29	**90**
Ti 336.122	53.6	4.73	98.8	1.94	**90**
V 292.401	<MDL	-	52.8	2.08	**106**

The digested solutions were further diluted by 1:2 V/V with water to lower their acid concentration prior to ICP OES analysis. The final spiked concentration was 50 µg/L.

CATHODE MATERIALS

6.4.8 **NCA – Lithium Nickel Cobalt Aluminum Oxide**

Lithium nickel cobalt aluminum oxide battery ($LiNiCoAlO_2$), cathode material, shares similarities with NMC by offering high specific energy, reasonably good specific power and a long lifespan. Less flattering are safety and cost. NCA is a further development of lithium nickel oxide; adding aluminum improves stability.
The purposes of NCA analysis are 1) to determine the composition of the main elements (QC/Production) and 2) to evaluate the purity of the raw material (QC/R&D).

■ Method for **ETHOS UP**

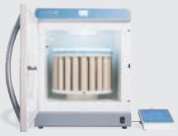
SAMPLE MASS
500 mg

FINAL VOLUME
50 mL

REAGENTS
2 mL of HNO_3 and 6 mL of HCl

MICROWAVE HEATING PROGRAM

	Time	*Temp*	*Power*
1	25 min	230°C	1800 W
2	15 min	230°C	1800 W



■ Method for **ultraWAVE**

SAMPLE MASS
500 mg

FINAL VOLUME
50 mL

REAGENTS
1 mL of HNO_3 + 3 mL of HCl

MICROWAVE HEATING PROGRAM

	Time	*T1*	*T2*	*Power*	*P*
1	15 min	250°C	60°C	1500 W	40 bar
2	20 min	250°C	60°C	1500 W	40 bar

Spike recoveries and Internal standard

Spike standard. Three replicates out of six were spiked with 500 µL of periodic table mix 1 (solution h) and 2 (solution i) for ICP standards respectively, immediately after sample weighing and prior to reagent addition. These worked as recovery studies for elemental impurities.
The concentration of the spiked elements in the final digested solution was 100 µg/L.
Internal standard. 10 µg/mL of Yttrium standard (d) was added to calibration standards, blanks, digested solutions and, where appropriate, to their dilutions (e.g.: 500 µL of Y std added to 50 mL of digested solution). This was used as internal standard to correct matrix effects.

Method **Results**

Major elements in NCA sample

	Determined concentration	*RSD (n = 6)*
Al 396.152	1.09 %	1.72 %
Co 238.892	6.54 %	0.65 %
Li 670.783	8.58 %	0.68 %
Ni 216.555	55.2 %	4.49 %

Impurities and spike recoveries in NCA sample

	Determined concentration (µg/L)	*RSD% (n = 3)*	*Spiked determined concentration (µg/L)*	*RSD% (n=3)*	**Spike recovery (%)**
Ag 328.068	<MDL	-	81.5	8.11	**102**
As 188.980	<MDL	-	81.8	2.15	**102**
Ba 455.403	<MDL	-	75.03	2.39	**94**
Be 313.042	<MDL	-	75.8	3.72	**95**
Cd 214.439	<MDL	-	71.7	2.67	**90**
Cr 267.716	<MDL	-	73.8	3.88	**92**
Cu 324.754	<MDL	-	74.3	1.41	**93**
Fe 238.204	65.9	1.93	138	1.82	**91**
Mn 257.610	<MDL	-	77.0	3.48	**96**
Mo 202.032	<MDL	-	72.5	3.77	**91**
Na 588.995	13.5	15.2	95.7	3.90	**103**
Nb 309.417	71.9	0.29	143	3.51	**89**
Pb 182.143	<MDL	-	91.9	4.44	**115**
Se 196.026	15.5	3.77	89.5	6.55	**93**
Sn 189.925	<MDL	-	75.9	5.26	**95**
Sr 407.771	12.6	0.56	86.2	3.18	**92**
Ti 334.941	<MDL	-	71.7	2.39	**90**
V 292.401	25.3	1.96	97.1	2.68	**90**
Zn 206.200	11.4	265	86.3	1.54	**94**

The digested solutions were further diluted by 1:2 V/V with water to lower their acid concentration prior to ICP OES analysis. The final spiked concentration was 50 µg/L.

CATHODE MATERIALS

6.4.9 **LFP – Lithium Iron Phosphate**

Lithium iron phosphate, $LiFePO_4$ (LFP), is extensively used in the lithium-ion battery field as cathode material. The main advantages of LFP are its flat voltage profile, low material cost, abundant material supply and better environmental compatibility compared to other cathode materials. In fact, LFP contains neither nickel nor cobalt, both of which are supply-constrained and expensive. The use of phosphates avoids cobalt's cost and environmental concerns.
The purposes of LFP analysis are 1) to determine the composition of the main elements (QC/Production) and 2) to evaluate the purity of the raw material (QC/R&D).

■ Method for **ETHOS UP**

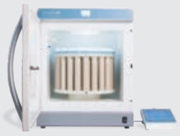
SAMPLE MASS
500 mg

FINAL VOLUME
50 mL

REAGENTS
2 mL of HNO_3 + 6 mL of HCl

MICROWAVE HEATING PROGRAM

	Time	*Temp*	*Power*
1	25 min	230°C	1800 W
2	15 min	230°C	1800 W



■ Method for **ultraWAVE**

SAMPLE MASS
500 mg

FINAL VOLUME
50 mL

REAGENTS
1 mL of HNO_3 + 3 mL of HCl

MICROWAVE HEATING PROGRAM

	Time	*T1*	*T2*	*Power*	*P*
1	15 min	250°C	60°C	1500 W	40 bar
2	20 min	250°C	60°C	1500 W	40 bar

Spike recoveries and Internal standard

Spike standard. Three replicates out of six were spiked with 1000 µL of periodic table mix 1 (solution h) and 2 (solution i) for ICP standards respectively, immediately after sample weighing and prior to reagent addition. These worked as recovery studies for elemental impurities.
The concentration of the spiked elements in the final digested solution was 200 µg/L.
Internal standard. 10 µg/mL of Yttrium standard (d) was added to calibration standards, blanks, digested solutions and, where appropriate, to their dilutions (e.g.: 500 µL of Y std added to 50 mL of digested solution). This was used as internal standard to correct matrix effects.

■ Method **Results**

Major elements in LFP sample

	Determined concentration	*RSD (n = 6)*
Li 670.783	4.81 %	1.38 %
Fe 238.204	33.9 %	1.65 %
P 213.618	20.2 %	4.01 %
Ca 396.847	0.47 %	4.55 %
K 766.491	84.4 mg/kg	3.54 %
Mg 279.553	8.29 mg/kg	5.80 %
Na 589.592	55.7 mg/kg	4.32 %

Impurities and spike recoveries in LFP sample

	Determined concentration (µg/L)	*RSD% (n = 3)*	*Spiked determined concentration (µg/L)*	*RSD% (n=3)*	**Spike recovery (%)**
Ag 328.068	26.5	21.3	120	7.94	**93**
Al 237.312	16.6	2.45	121	1.34	**105**
As 193.696	72.1	10.4	179	1.79	**106**
Ba 455.403	<MDL	-	95.8	1.81	**96**
Be 313.107	<MDL	-	93.3	3.67	**93**
Cd 214.439	45.7	11.4	144	2.48	**98**
Co 238.892	<MDL	-	94.4	0.86	**94**
Cr 206.158	38.5	16.2	144	1.78	**105**
Cu 324.754	<MDL	-	95.0	0.56	**95**
Mo 202.032	<MDL	-	98.4	1.61	**98**
Ni 231.604	<MDL	-	91.9	0.68	**92**
Nb 313.078	<MDL	-	94.4	1.71	**94**
Pb 182.143	<MDL	-	97.3	0.84	**97**
Ru 240.272	76.9	7.4	169	3.70	**93**
Sb 206.834	<MDL	-	93.8	1.30	**94**
Sr 407.771	<MDL	-	95.6	3.35	**96**
Ti 336.122	<MDL	-	93.1	2.77	**93**
V 292.401	92.4	2.83	210	4.15	**118**
Zn 206.200	263	8.35	359	4.63	**97**

The digested solutions were further diluted by 1:2 V/V with water to lower their acid concentration prior to ICP OES analysis. The final spiked concentration was 100 µg/L.

CATHODE MATERIALS

6.4.10 **LMO – Lithium Manganese Oxide**

Li-ion batteries with Lithium manganese oxide ($LiMn_2O_4$) as cathode material were commercialized since 1996. LMO was used for its higher power capabilities and safety compared to Li-cobalt, but it has a lower capacity compared to Li-cobalt.

Pure Li-manganese batteries are no longer common today; they may only be used for special applications, but this material is often used in combination with other materials, i.e. NMC, to obtain higher technical specifications.

The purposes of LMO analysis are 1) to determine the composition of the main elements (QC/Production) and 2) to evaluate the purity of the raw material (QC/R&D).

■ Method for **ETHOS UP**

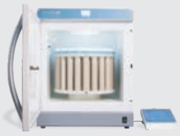
SAMPLE MASS
500 mg

FINAL VOLUME
50 mL

REAGENTS
2 mL of HNO_3 + 6 mL of HCl

MICROWAVE HEATING PROGRAM

	Time	*Temp*	*Power*
1	25 min	230°C	1800 W
2	15 min	230°C	1800 W



■ Method for **ultraWAVE**

SAMPLE MASS
500 mg

FINAL VOLUME
50 mL

REAGENTS
1 mL of HNO_3 + 3 mL of HCl

MICROWAVE HEATING PROGRAM

	Time	*T1*	*T2*	*Power*	*P*
1	15 min	250°C	60°C	1500 W	40 bar
2	20 min	250°C	60°C	1500 W	40 bar

Spike recoveries and Internal standard

Spike standard. Three replicates out of six were spiked with 800 µL of periodic table mix 1 (solution h) and 2 (solution i) for ICP standards respectively, immediately after sample weighing and prior to reagent addition. These worked as recovery studies for elemental impurities.

The concentration of the spiked elements in the final digested solution was 160 µg/L.

Internal standard. 10 µg/mL of Yttrium standard (d) was added to calibration standards, blanks, digested solutions and, where appropriate, to their dilutions (e.g.: 500 µL of Y std added to 50 mL of digested solution). This was used as internal standard to correct matrix effects.

■ Method **Results**

Major elements in LMO sample

	Determined concentration	*RSD (n = 6)*
Li 670.783	4.82 %	1.46 %
Mn 257.610	61.8 %	5.05 %

Impurities and spike recoveries in LMO sample

	Determined concentration (µg/L)	*RSD% (n = 3)*	*Spiked determined concentration (µg/L)*	*RSD% (n=3)*	Spike recovery (%)
As 188.980	161	0.62	259	2.49	**122**
Ba 455.403	4.31	3.29	79.6	2.79	**94**
Be 313.042	<MDL	-	77.8	2.71	**97**
Bi 223.061	176	0.66	263	1.87	**110**
Cd 214.439	<MDL	-	78.6	3.60	**98**
Cu 324.754	<MDL	-	83.8	5.05	**105**
Fe 234.350	166	1.20	261	0.59	**118**
Ir 212.681	<MDL	-	77.1	3.38	**96**
Mo 202.032	<MDL	-	90.9	2.26	**114**
Pb 182.143	<MDL	-	80.2	7.78	**100**
Rb 421.552	14.7	2.39	89.2	2.60	**93**
Sb 217.582	152	3.24	243	4.18	**113**
Sn 189.925	<MDL	-	84.7	5.86	**106**
Sr 407.771	14.3	2.83	90.3	2.92	**95**
Te 214.282	75.7	2.67	163	1.06	**109**
Ti 334.941	103	3.64	197	1.93	**117**
V 292.401	<MDL	-	73.9	3.57	**92**
Zn 206.200	12.9	1.62	87.5	2.03	**93**

The digested solutions were further diluted by 1:2 V/V with water to lower their acid concentration prior to ICP OES analysis. The final spiked concentration was 80 µg/L.

CATHODE MATERIALS

6.4.11 LNMO – Lithium Nickel Manganese Oxide

LNMO is a new generation of lithium-ion battery cathode material. High-voltage lithium nickel manganese oxide (LiNi0.5Mn1.5O_4) is suitable for various lithium-ion batteries and it has several advantages: high voltage, long lifecycle, good rate performance and high energy density.
The purposes of LNMO analysis are 1) to determine the composition of the main elements (QC/Production) and 2) to evaluate the purity of the raw material (QC/R&D).

■ Method for **ETHOS UP**

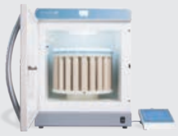
SAMPLE MASS
500 mg

FINAL VOLUME
50 mL

REAGENTS
2 mL of HNO_3 + 6 mL of HCl

MICROWAVE HEATING PROGRAM

	Time	*Temp*	*Power*
1	25 min	230°C	1800 W
2	15 min	230°C	1800 W



■ Method for **ultraWAVE**

SAMPLE MASS
500 mg

FINAL VOLUME
50 mL

REAGENTS
1 mL of HNO_3 + 3 mL of HCl

MICROWAVE HEATING PROGRAM

	Time	*T1*	*T2*	*Power*	*P*
1	15 min	250°C	60°C	1500 W	40 bar
2	20 min	250°C	60°C	1500 W	40 bar

Spike recoveries and Internal standard

Spike standard. Three replicates out of six were spiked with 1000 µL of periodic table mix 1 (solution h) and 2 (solution i) for ICP standards respectively, immediately after sample weighing and prior to reagent addition. These worked as recovery studies for elemental impurities.
The concentration of the spiked elements in the final digested solution was 200 µg/L.
Internal standard. 10 µg/mL of Yttrium standard (d) was added to calibration standards, blanks, digested solutions and, where appropriate, to their dilutions (e.g.: 500 µL of Y std added to 50 mL of digested solution). This was used as internal standard to correct matrix effects.

Method **Results**

Major elements in LNMO sample

	Determined concentration	RSD (n = 6)
Li 670.783	3.95 %	2.39 %
Mn 257.610	44.3 %	2.33 %
Ni 231.604	16.2 %	2.67 %
Co 238.892	794 mg/kg	3.86 %
Fe 238.204	150 mg/kg	6.01 %
Si 251.611	220 mg/kg	3.96 %

Impurities and spike recoveries in LNMO sample

	Determined concentration (µg/L)	RSD% (n = 3)	Spiked determined concentration (µg/L)	RSD% (n=3)	Spike recovery (%)
Ag 328.068	443	5.34	551	3.49	**107**
Al 237.312	377	5.84	471	3.08	**94**
As 193.696	182	6.61	272	4.09	**90**
B 249.772	162	4.95	263	3.60	**101**
Ba 455.403	208	5.05	299	3.23	**91**
Be 313.107	<MDL	-	95.1	1.94	**95**
Bi 223.061	127	4.04	223	2.08	**95**
Cd 214.439	<MDL	-	94.6	2.33	**95**
Cr 206.158	108	4.66	208	4.88	**101**
Cu 324.754	21.8	8.96	123	7.59	**101**
Mo 202.032	28.1	1.63	121	4.97	**93**
Nb 313.078	<MDL	-	96.0	3.92	**96**
Pb 182.143	54.4	7.54	158	5.27	**103**
Ru 240.272	<MDL	-	92.0	1.87	**92**
Sb 206.834	36.0	4.05	130	4.01	**94**
Sr 407.771	86.5	5.48	179	2.97	**92**
Ti 336.122	563	5.35	657	4.87	**95**
Tl 351.923	61.2	13.0	190	3.80	**129**
V 292.401	49.1	3.96	141	2.16	**92**
Zn 206.200	43.2	1.49	139	2.78	**96**

The digested solutions were further diluted by 1:2 V/V with water to lower their acid concentration prior to ICP OES analysis. The final spiked concentration was 100 µg/L.

ANODE MATERIALS

6.4.12 **Graphite**

Graphite, the most stable allotropic form of carbon, is still the dominant active anode material for Li-ion batteries. The performance of graphite as a safe and reliable material that provides sufficient energy density for many portable power applications, such as mobile phones and laptop computers, explains this dominance.
For Li-ion battery production, the key factor is the purity of graphite, which must be more than 99.0%.
Graphite comes in two forms: natural graphite from mines and synthetic graphite from petroleum coke. Both types are used for Li-ion anode material but in the last few years the market is gravitating toward the natural one because it is less expensive and more environmentally-friendly compared to the synthetic form.
The main purpose of graphite analysis is to evaluate the purity of the raw material (QC/R&D).

■ Method for **ETHOS UP**

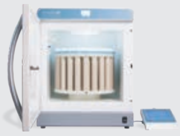
SAMPLE MASS
200 mg

FINAL VOLUME
50 mL

REAGENTS
6 mL of H_2SO_4 + 4 mL of $HClO_4$
+ 500 µL of Vanadium std solution (1000 mg/L)*

MICROWAVE HEATING PROGRAM

	Time	*Temp*	*Power*
1	25 min	240°C	1800 W
2	60 min	240°C	1800 W



** Vanadium works as a catalyst to efficiently breaking the C-C bonds of graphite.*

■ Method for **ultraWAVE**

SAMPLE MASS
200 mg

FINAL VOLUME
50 mL

REAGENTS
3 mL of H_2SO_4 + 2 mL of $HClO_4$
+ 500 µL of Vanadium std solution (1000 mg/L)*

MICROWAVE HEATING PROGRAM

	Time	*T1*	*T2*	*Power*	*P*
1	15 min	280°C	60°C	1500 W	50 bar
2	60 min	280°C	60°C	1500 W	50 bar

** Vanadium works as a catalyst to efficiently breaking the C-C bonds of graphite.*

Spike recoveries and Internal standard

Spike standard. Three replicates out of six were spiked with 250 µL of periodic table mix 1 (solution h) and 2 (solution i) for ICP standards respectively, immediately after sample weighing and prior to reagent addition. These worked as recovery studies for elemental impurities.
The concentration of the spiked elements in the final digested solution was 50 µg/L.

Internal standard. 10 µg/mL of Yttrium standard (d) was added to calibration standards, blanks, digested solutions and, where appropriate, to their dilutions (e.g.: 500 µL of Y std added to 50 mL of digested solution). This was used as internal standard to correct matrix effects.

■ Method **Results**

Impurities and spike recoveries in Natural Graphite sample

	Determined concentration (µg/L)	*RSD% (n = 3)*	*Spiked determined concentration (µg/L)*	*RSD% (n=3)*	**Spike recovery (%)**
Ag 328.068	15.5	7.40	61.0	7.57	**91**
Al 396.152	48.9	6.29	96.7	4.58	**96**
As 193.696	109	7.20	165	2.26	**114**
Ba 455.403	<MDL	-	54.9	2.69	**110**
Be 313.107	<MDL	-	47.7	2.70	**95**
Bi 223.061	<MDL	-	46.3	5.11	**93**
Cd 214.439	<MDL	-	47.7	1.94	**95**
Co 238.892	58.7	4.78	107	0.88	**96**
Cr 267.716	48.6	8.11	102	1.44	**107**
Cu 324.754	24.9	7.2	78.9	2.94	**108**
K 766.491	58.0	4.8	106	8.30	**95**
Li 670.783	32.2	2.29	89.5	0.72	**115**
Mg 279.553	50.1	2.89	96.3	2.00	**92**
Mn 257.610	<MDL	-	49.6	3.85	**99**
Mo 202.032	54.1	1.71	106	0.76	**103**
Ni 231.604	<MDL	-	54.6	3.53	**109**
P 213.618	71.1	4.50	123	8.94	**103**
Pb 220.353	<MDL	-	47.4	5.80	**95**
Rb 421.552	<MDL	-	51.1	2.96	**102**
Ti 336.122	75.3	2.23	125	1.44	**99**
Zn 213.857	<MDL	-	45.9	5.62	**92**

ANODE MATERIALS

6.4.13 **LTO – Lithium Titanate Oxide**

Lithium titanate oxide ($Li_4Ti_5O_{12}$) replaces the graphite in the anode of a typical lithium-ion battery. In this case, the cathode can be LMO or NMC. The use of LTO as anode material gives several advantages to Li-ion battery: long life, fast charge, wide working temperature range and good safety. The main drawback is its high cost.
The purposes of LTO analysis are 1) to determine the composition of the main elements (QC/Production) and 2) to evaluate the purity of the raw material (QC/R&D).

■ Method for **ETHOS UP**

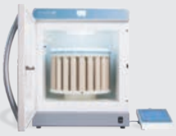
SAMPLE MASS
500 mg

FINAL VOLUME
50 mL

REAGENTS
5 mL of HNO_3 + 1 mL of HF

MICROWAVE HEATING PROGRAM

	Time	*Temp*	*Power*
1	25 min	230°C	1800 W
2	15 min	230°C	1800 W



■ Method for **ultraWAVE**

SAMPLE MASS
500 mg

FINAL VOLUME
50 mL

REAGENTS
5 mL of HNO_3 + 1 mL of HF

MICROWAVE HEATING PROGRAM

	Time	*T1*	*T2*	*Power*	*P*
1	15 min	270°C	60°C	1500 W	40 bar
2	30 min	270°C	60°C	1500 W	40 bar

Spike recoveries and Internal standard

Spike standard. Three replicates out of six were spiked with 1000 µL of periodic table mix 1 (solution h) and 2 (solution i) for ICP standards respectively, immediately after sample weighing and prior to reagent addition. These worked as recovery studies for elemental impurities.
The concentration of the spiked elements in the final digested solution was 200 µg/L.
Internal standard. 10 µg/mL of Yttrium standard (d) was added to calibration standards, blanks, digested solutions and, where appropriate, to their dilutions (e.g.: 500 µL of Y std added to 50 mL of digested solution). This was used as internal standard to correct matrix effects.

■ Method **Results**

Major elements in LTO sample

	Determined concentration	*RSD (n = 6)*
Li 670.783	6.17 %	1.04 %
Ti 336.122	48.3 %	2.44 %

Impurities and spike recoveries in LTO sample

	Determined concentration (µg/L)	*RSD% (n = 3)*	*Spiked determined concentration (µg/L)*	*RSD% (n=3)*	Spike recovery (%)
Ag 328.068	<MDL	-	92.7	0.83	**93**
Al 237.312	187	5.14	288	6.88	**101**
As 193.696	112	6.52	207	3.14	**96**
Ba 455.403	98.3	5.75	196	1.06	**98**
Be 313.107	104	2.64	200	4.11	**96**
Cd 214.439	<MDL	-	98.3	4.58	**98**
Co 238,892	<MDL	-	93.7	2.44	**94**
Cr 206.158	209	3.23	322	8.09	**113**
Cu 324.754	164	1.84	254	1.38	**90**
Mg 279.553	111	7.24	223	2.69	**112**
Mn 279.553	<MDL	-	97.1	0.99	**97**
Mo 202.032	23.7	9.01	118	1.85	**94**
Ni 231.604	51.5	2.52	156	1.70	**105**
Pb 217.000	<MDL	-	91.6	1.56	**92**
Se 196.026	<MDL	-	91.3	2.77	**91**
Si 251.611	<MDL	-	91.6	1.53	**91**
Sn 189.925	<MDL	-	91.9	3.02	**92**
Sr 407.771	<MDL	-	94.3	0.61	**94**
V 292.401	20.3	4.93	110	0.94	**90**
Zn 213.857	<MDL	-	91.6	2.12	**91**

The digested solutions were further diluted by 1:2 V/V with water to lower their acid concentration prior to ICP OES analysis. The final spiked concentration was 100 µg/L.

ANODE MATERIALS

6.4.14 **Silicon Oxides (SiOx)**

Silicon oxides have been recognized as a promising family of anode materials for high-energy lithium-ion batteries owing to their abundant reserve, low cost, environmental friendliness, easy synthesis, and high theoretical capacity. However, the extended application of silicon oxides is severely hampered by the intrinsically low conductivity, large volume change, and low initial coulombic efficiency. Significant efforts have been dedicated to tackling these challenges towards practical applications.

■ Method for **ETHOS UP**

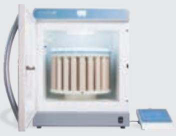
SAMPLE MASS
200 mg

FINAL VOLUME
50 mL

REAGENTS
5 mL of HNO_3 + 1 mL of HF

MICROWAVE HEATING PROGRAM

	Time	*Temp*	*Power*
1	25 min	230°C	1800 W
2	15 min	230°C	1800 W



■ Method for **ultraWAVE**

SAMPLE MASS
200 mg

FINAL VOLUME
50 mL

REAGENTS
3 mL of HNO_3 + 1 mL of HF

MICROWAVE HEATING PROGRAM

	Time	*T1*	*T2*	*Power*	*P*
1	15 min	250°C	60°C	1500 W	40 bar
2	30 min	250°C	60°C	1500 W	40 bar

Spike recoveries and Internal standard

Spike standard. Three replicates out of six were spiked with 800 µL of periodic table mix 1 (solution h) and 2 (solution i) for ICP standards respectively, immediately after sample weighing and prior to reagent addition. These worked as recovery studies for elemental impurities.
The concentration of the spiked elements in the final digested solution was 160 µg/L.
Internal standard. 10 µg/mL of Yttrium standard (d) was added to calibration standards, blanks, digested solutions and, where appropriate, to their dilutions (e.g.: 500 µl of Y std added to 50 mL of digested solution). This was used as internal standard to correct matrix effects.

Method **Results**

Major elements in SiO sample

	Determined concentration	*RSD (n = 6)*
Si 251.611	61.1 %	1.27 %

Impurities and spike recoveries in SiO sample

	Determined concentration (%)	*RSD% (n = 3)*	*Spiked determined concentration (%)*	*RSD% (n=3)*	**Spike recovery (%)**
Ag 328.068	<MDL	-	28.9	1.93	**90**
Al 396.152	36.8	4.42	70.5	0.57	**105**
As 188.980	<MDL	-	30.7	4.98	**96**
Ba 455.403	<MDL	-	30.3	1.51	**95**
Be 234.861	<MDL	-	28.9	1.59	**90**
Bi 223.061	<MDL	-	30.9	5.58	**96**
Ca 396.847	98.0	5.47	127	1.57	**91**
Cd 214.439	<MDL	-	28.8	2.51	**90**
Co 228.615	<MDL	-	28.8	5.38	**90**
Cr 267.716	<MDL	-	30.1	4.28	**94**
Cu 327.395	<MDL	-	33.0	0.46	**103**
Fe 238.204	44.8	5.21	78.9	2.23	**106**
K 769.897	<MDL	-	34.5	5.70	**108**
Li 670.783	<MDL	-	29.8	3.54	**93**
Mg 279.553	<MDL	-	35.0	3.00	**109**
Mn 257.610	20.6	0.74	51.3	2.24	**96**
Mo 203.846	<MDL	-	28.3	2.66	**88**
Nb 313.078	<MDL	-	28.8	4.51	**90**
Ni 231.604	<MDL	-	31.7	5.79	**99**
Pb 220.353	<MDL	-	28.3	2.97	**88**
Rb 421.552	<MDL	-	30.5	4.19	**95**
Sb 206.834	<MDL	-	29.6	6.60	**93**
Se 196.026	<MDL	-	29.8	4.51	**93**
Sn 189.925	<MDL	-	29.4	7.82	**92**
Sr 407.771	<MDL	-	30.2	2.32	**94**
Te 214.282	<MDL	-	31.1	6.13	**97**
Ti 336.122	<MDL	-	28.9	2.61	**90**
V 292.401	<MDL	-	30.8	4.50	**96**
Zn 213.857	<MDL	9.53	41.3	1.96	**91**

The digested solutions were further diluted by 1:5 V/V with water to lower their acid concentration prior to ICP OES analysis. The final spiked concentration was 32 µg/L.

ANODE MATERIALS

6.4.15 **Graphene Nanotubes**

Graphene nanotubes, or single-wall carbon nanotubes, are hugely recognized as a “wonder material” due to the myriad of astonishing attributes graphene holds. In the field of batteries, conventional battery electrode materials (and prospective ones) are significantly improved when enhanced with graphene. A graphene battery can be light, durable and suitable for high-capacity energy storage, as well as shorten charging times. It will extend the battery’s life, which is negatively linked to the amount of carbon that is coated on the material or added to electrodes to achieve conductivity, and graphene adds conductivity without requiring the amounts of carbon that are used in conventional batteries.

Method for **ETHOS UP**

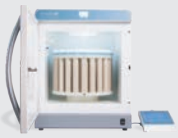
SAMPLE MASS
1000 mg (0.2-0.4% dispersion in water)

FINAL VOLUME
50 mL

REAGENTS
3 mL of H_2SO_4 + 2 mL of $HClO_4$
+ 500 µl of Vanadium std solution (1000 mg/L)[*]

MICROWAVE HEATING PROGRAM

	Time	Temp	Power
1	25 min	230°C	1800 W
2	15 min	230°C	1800 W



** Vanadium works as a catalyst to efficiently breaking the C-C bonds.*

Method for **ultraWAVE**

SAMPLE MASS
1000 mg (0.2-0.4% dispersion in water)

FINAL VOLUME
50 mL

REAGENTS
3 mL of H_2SO_4 + 2 mL of $HClO_4$[**]

MICROWAVE HEATING PROGRAM

	Time	T1	T2	Power	P
1	20 min	270°C	60°C	1500 W	40 bar
2	30 min	270°C	60°C	1500 W	40 bar

*** Due to the higher temperature capabilities, the use of vanadium in ultraWAVE can be avoided.*

Spike recoveries and Internal standard

Spike standard. Three replicates out of six were spiked with 800 µL of periodic table mix 1 (solution h) and 2 (solution i) for ICP standards respectively, immediately after sample weighing and prior to reagent addition. These worked as recovery studies for elemental impurities.
The concentration of the spiked elements in the final digested solution was 160 µg/L.
Internal standard. 10 µg/mL of Yttrium standard (d) was added to calibration standards, blanks, digested solutions and, where appropriate, to their dilutions (e.g.: 500 µl of Y std added to 50 mL of digested solution). This was used as internal standard to correct matrix effects.

■ Method **Results**

Impurities and spike recoveries in graphene carbon nanotubes sample

	Determined concentration (%)	*RSD% (n = 3)*	*Spiked determined concentration (%)*	*RSD% (n=3)*	**Spike recovery (%)**
Ag 328.068	15.7	3.18	163	4.02	**92**
Al 396.152	212	1.51	377	0.81	**103**
As 188.980	<MDL	-	221	4.99	**138**
Ba 455.403	<MDL	-	166	0.94	**102**
Be 234.861	<MDL	-	163	1.62	**102**
Bi 223.061	<MDL	-	148	2.72	**93**
Cd 214.439	<MDL	-	164	0.35	**103**
Co 228.615	<MDL	-	161	0.36	**101**
Cr 267.716	22.2	1.60	163	4.02	**97**
Cu 327.395	<MDL	-	161	0.36	**100**
Fe 238.204	324	1.29	499	1.67	**110**
Li 670.783	<MDL	-	167	0.91	**105**
Mn 257.610	<MDL	-	151	0.66	**94**
Mo 203.846	<MDL	-	169	2.05	**106**
Ni 231.604	<MDL	-	161	1.29	**101**
Pb 220.353	<MDL	-	161	1.56	**101**
Rb 421.552	10.0	2.83	170	0.90	**100**
Sb 206.834	<MDL	-	154	2.46	**96**
Se 196.026	<MDL	-	207	2.29	**120**
Sn 189.925	14.4	2.21	182	1.98	**114**
Sr 407.771	<MDL	-	169	1.49	**99**

The digested solutions were further diluted by 1:5 V/V with water to lower their acid concentration prior to ICP OES analysis. The final spiked concentration was 32 µg/L.

ELECTROLYTE

6.4.16 **$LiPF_6$ – Lithium Hexafluorophosphate**

Lithium hexafluorophosphate ($LiPF_6$) is the most widely used salt in the electrolytes for lithium-ion cells. Liquid electrolyte solutions play a key role acting as carrier of lithium ions between the cathode and anode. High-purity and battery-grade electrolyte solutions are thus crucial for lithium-ion battery performances.
$LiPF_6$ is highly soluble in non-aqueous, polar solvents and, at these conditions, the inertness of hexafluorophosphate anion toward strong reducing agents, such as lithium metal, can be exploited. Lithium hexafluorophosphate solution in carbonate blends of ethylene carbonate, dimethyl carbonate, diethyl carbonate and/or ethyl methyl carbonate, with a small amount of one or many additives serve as state-of-the-art electrolytes in lithium-ion batteries.

Method for **ETHOS UP**

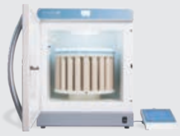
SAMPLE MASS
1000 mg $LiPF_6$ (1M solution in EC:DMC:DEC 1:1:1)*

FINAL VOLUME
25 mL

REAGENTS
4 mL of HNO_3 + 2 mL of DD water

MICROWAVE HEATING PROGRAM

	Time	*Temp*	*Power*
1	15 min	180°C	1800 W
2	20 min	180°C	1800 W



Method for **ultraWAVE**

SAMPLE MASS
2000 mg $LiPF_6$ (1M solution in EC:DMC:DEC 1:1:1)*

FINAL VOLUME
25 mL

REAGENTS
4 mL of HNO_3 + 2 mL of DD water

MICROWAVE HEATING PROGRAM

	Time	*T1*	*T2*	*Power*	*P*
1	10 min	200°C	60°C	1500 W	40 bar
2	10 min	200°C	60°C	1500 W	40 bar

Spike recoveries and Internal standard

Spike standard. Three replicates out of six were spiked with 500 µL of periodic table mix 1 (solution h) and 2 (solution i) for ICP standards respectively, immediately after sample weighing and prior to reagent addition. These worked as recovery studies for elemental impurities.
The concentration of the spiked elements in the final digested solution was 200 µg/L.
**For spiked samples, the reagent addition was performed as follows: 4 mL of nitric acid + 0.5 mL of multi-elemental standard (c) + 1.5 mL of double distilled water (b).*

The concentration of the spiked elements in the final digested solution was 160 µg/L.
Internal standard. 10 µg/mL of Yttrium standard (d) was added to calibration standards, blanks, digested solutions and, where appropriate, to their dilutions (e.g.: 500 µL of Y std added to 50 mL of digested solution). This was used as internal standard to correct matrix effects.

Method **Results**

Major elements in LiPF6 sample

	Determined concentration	*RSD (n = 6)*
Li 610.365	4.72 %	5.78 %
P 213.618	23.2 %	4.03 %

Impurities and spike recoveries in LiPF6 electrolyte sample

	Determined concentration (µg/L)	*RSD% (n = 3)*	*Spiked determined concentration (%)*	*RSD% (n=3)*	**Spike recovery (%)**
Ag 338.289	-	-	179	2.32	**90**
Al 396.152	29.6	3.05	211	1.66	**91**
As 188.980	-	-	250	3.12	**125**
B 249.678	-	-	190	1.21	**95**
Ba 493.408	-	-	188	0.81	**94**
Be 234.861	-	-	200	0.76	**100**
Bi 223.061	-	-	203	2.96	**102**
Cd 214.439	-	-	195	0.51	**98**
Co 228.615	-	-	182	1.27	**91**
Cr 205.560	-	-	201	7.72	**101**
Cu 324.754	-	-	184	1.37	**92**
Fe 259.940	-	-	196	1.06	**98**
Ir 212.681	-	-	208	0.28	**104**
Mg 280.270	14.2	5.64	201	2.51	**93**
Mn 257.610	-	-	187	1.41	**94**
Mo 202.032	-	-	212	0.72	**106**
Na 589.592	216	6.48	454	2.42	**119**
Ni 231.604	-	-	190	1.90	**95**
Pb 220.353	-	-	183	1.14	**91**
Ru 267.876	-	-	175	0.87	**88**
S 181.972	-	-	234	5.59	**117**
Sb 206.834	-	-	215	1.17	**108**
Se 196.026	-	-	230	1.53	**115**
Sn 189.925	-	-	209	1.99	**105**
Sr 407.771	-	-	180	1.16	**90**
Ti 336.122	-	-	193	1.67	**96**
Tl 190.794	-	-	159	2.20	**80**
V 292.401	-	-	195	0.59	**97**
Zn 213.857	-	-	199	0.58	**100**

RECYCLING MATERIAL

6.4.17 **Black Mass**

Black mass is the name given to the powder substance obtained during the recycling process of end-of-life Li-ion batteries. In fact, after removing plastics, copper and aluminum to be recycled by more conventional methods, a sludgy mixture of valuable metals including lithium, manganese, cobalt, nickel and graphite is left behind for further recovery.

A more and more relevant interest and effort by recycling industries is put to find the most effective process to recover the utmost percentage of metals to be re-used in “second life” applications.

Black mass characterization can be easily performed by microwave-assisted acid digestion and ICP OES analysis.

■ Method for **ETHOS UP**

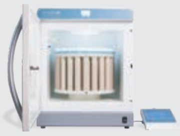
SAMPLE MASS
100 mg

FINAL VOLUME
50 mL

REAGENTS
3 mL of HNO_3 + 3 mL of H_2SO_4

MICROWAVE HEATING PROGRAM

	Time	*Temp*	*Power*
1	25 min	240°C	1800 W
2	60 min	240°C	1800 W



■ Method for **ultraWAVE**

SAMPLE MASS
100 mg

FINAL VOLUME
50 mL

REAGENTS
3 mL of HNO_3 + 3 mL of H_2SO_4

MICROWAVE HEATING PROGRAM

	Time	*T1*	*T2*	*Power*	*P*
1	25 min	280°C	60°C	1500 W	40 bar
2	30 min	280°C	60°C	1500 W	40 bar

Internal standard

10 µg/mL of Yttrium standard (d) was added to calibration standards, blanks, digested solutions and, where appropriate, to their dilutions (example: 500 µl of Y std added to 50 mL of digested solution). This was used as internal standard to correct matrix effects.

■ Method **Results**

Major elements in Black Mass sample

	Expected concentration (%)*	*Determined concentration (%)*	*RSD% (n = 6)*	**Recovery (%)**
Al 396.152	1.25	1.30	3.23	**105**
Co 238.892	21.6	22.0	1.46	**102**
Cu 327.395	2.79	2.85	5.85	**102**
Fe 238.204	0.24	0.27	5.45	**113**
Li 670.783	3.31	3.47	3.66	**105**
Mn 257.610	7.17	7.54	1.45	**105**
Ni 231.604	2.25	2.39	1.69	**106**

**The expected metal contents were determined by XRF analysis.*

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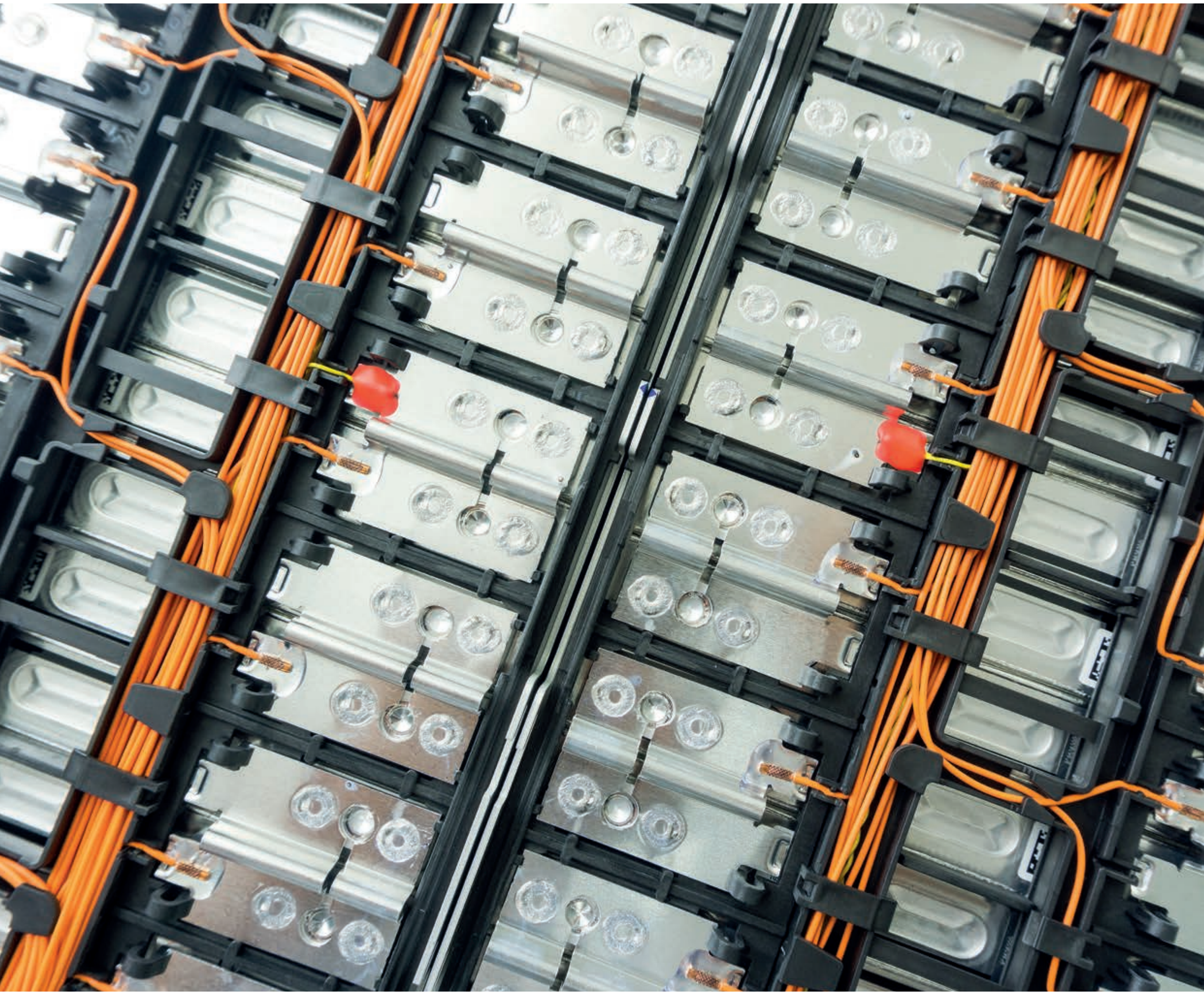

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