ELTRA®
ELEMENTAL ANALYZERS

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O/N AND C/S ANALYSIS OF BATTERY COMPONENTS

ENSURING QUALITY THROUGHOUT THE BATTERY LIFE CYCLE

Introduction

Modern life depends strongly on (mobile) electrical power, which is provided by batteries. No cellular phone, notebook, tablet or car could be operated without a proper working battery. Since Allesandro Volta first built and utilized a primary battery[1], a large number of batteries of various chemical compositions and different sizes has been developed which are used for a wide range of applications like flash lights or storage of excess electrical power from the grid or a power plant.

Regardless of the dimensions of a battery, its application or its configuration as primary (not rechargeable) or secondary battery (rechargeable), a chemical analysis for carbon, sulfur, oxygen or nitrogen may be required for single components. A reliable and precise measurement of C/S and O/N in selected samples over a wide concentration range is possible with elemental analyzers like the ELEMENTRAC CS-i and ONH-p2.

In contrast to spectrometric techniques like spark OES or XRF, which only measure the element concentration at the surface, the ELEMENTRAC series analyzers examine always the complete sample by combustion or inert gas fusion. This analysis principle assures a safe and reliable analysis from the lower ppm up to the high percentage range. The working principle of the analyzers and applications are described in the following.

[1] Wikipidea.org

Figure 1 : ELEMENTRAC ONH-p2 with optional autocleaner

The ELEMENTRAC ONH-p2 analyzer

The ELEMENTRAC ONH-p2 (Fig. 1) is a powerful inert gas fusion analyzer featuring an 8.5 kW electrode furnace, two infrared cells and a wide-range thermal conductivity cell for safe and reliable analysis of oxygen, nitrogen and hydrogen. Performing an analysis is easy and convenient for trained and untrained users alike.

The sample is logged in the ELEMENTS software with its weight, followed by the application to the sample port and starting of the measurement in the software. All other steps are done automatically.

After analysis start in the software the sample port closes and the sample is flushed with carrier gas which prevents atmospheric gas (oxygen and nitrogen) from getting into the furnace. Meanwhile a graphite crucible is outgassed in the impulse furnace of the analyzer to remove possible contaminations. After a short stabilization phase the sample is dropped into the crucible and melts. Due to the vertical sample transfer to the crucible (Fig. 2) and the effective flushing, the sealing of capsules containing a powdered sample is not required. This simplifies the whole analysis process of any powdered samples.

In the following carbon monoxide is produced by the reaction of carbon in the graphite crucible and oxygen of the sample. Nitrogen and hydrogen are released in its elemental form. The carrier gas (helium) and sample gasses pass through a filter before entering a copper oxide catalyst which converts the CO to CO_2.

The CO_2 is measured by the infrared cells to determine the oxygen content. CO_2 and water are removed chemically, and the nitrogen content is measured in the thermal conductivity cell. In the case of hydrogen analysis, nitrogen carrier as well as sample gas pass through a Schuetze reagent instead of a copper oxide catalyst. Optionally, less expensive Argon can be used to determinate the oxygen and nitrogen content during analysis.

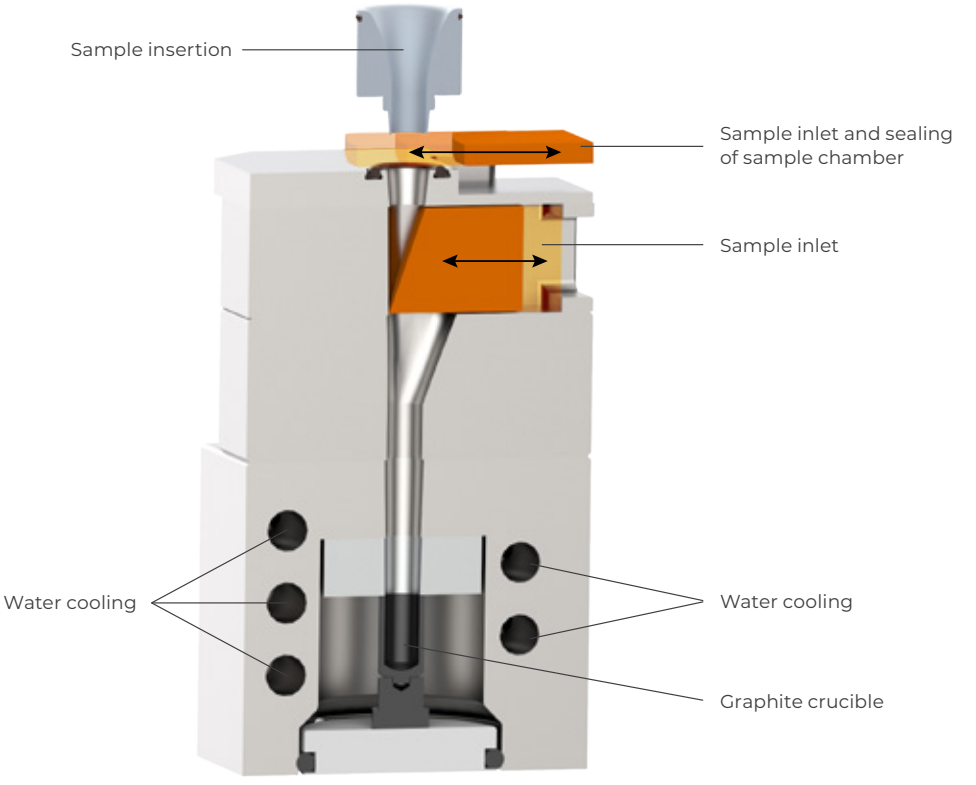


Figure 2: Sample port of the ELEMENTRAC ONH-p2

Figure 3: ELEMENTRAC CS-i

The ELEMENTRAC CS-i Analyzer

The elemental analyzer ELEMENTRAC CS-i (Fig. 3) measures the carbon and sulfur concentration in predominantly inorganic samples through combustion in an induction furnace and the subsequent analysis of the gaseous combustion products carbon dioxide and sulfur dioxide in up to 4 infrared cells.

The high temperature of more than 2000 °C ensures complete decomposition of the sample and thus reliable and accurate elemental analysis over a wide concentration range. After weighing a sample in a ceramic crucible, logging in the sample the ELEMENTS software, an accelerator like tungsten (approx. 1.7 g) must be added. After placing the sample on the pedestal and starting the analysis, all further steps are processed automatically. In the induction furnace of the elemental analyzer the sample and accelerator are melted in a pure oxygen atmosphere, causing sulfur to react to sulfur dioxide (SO_2) and carbon to a mixture of carbon monoxide (CO) and carbon dioxide (CO_2). The combustion gases pass through a dust filter and moisture absorber for purification. In the next step the sulfur dioxide is detected in infrared cells. In the CS-i infrared cells with different sensitivities (high/low) can be adapted according to the user's requirements. Oxidation of both, carbon monoxide to carbon dioxide and sulfur dioxide to sulfur trioxide follow the sulfur measurement. The SO_3 gas is subsequently removed with cellulose wool and the carbon content is detected by infrared cells.

Sample preparation

Elemental analyzers can measure C/S or O/N/H concentrations in almost any inorganic sample. Although the analysis process as such is pretty straightforward for C/S and O/NH measurement, some important details have to be considered, depending on the required analysis, sample shape and sample composition (see diagram below). Typical applicable sample weights for C/S and O/N/H analysis range between 20 and 1000 mg.

Sample-related settings and preparation for ONH analysis

For each battery component (e.g. Si3N4), an individual application has to be developed first which takes into account the available sample amount, the chemical nature of the sample, as well as the particle size and shape. These specifications determine the suitable maximum amount of sample for a single analysis, the required sample preparation and of course the applied analysis power. The following diagram illustrates the general procedure for powdered sample. Solid samples like wires or pins can be processed like drillings or granulates.

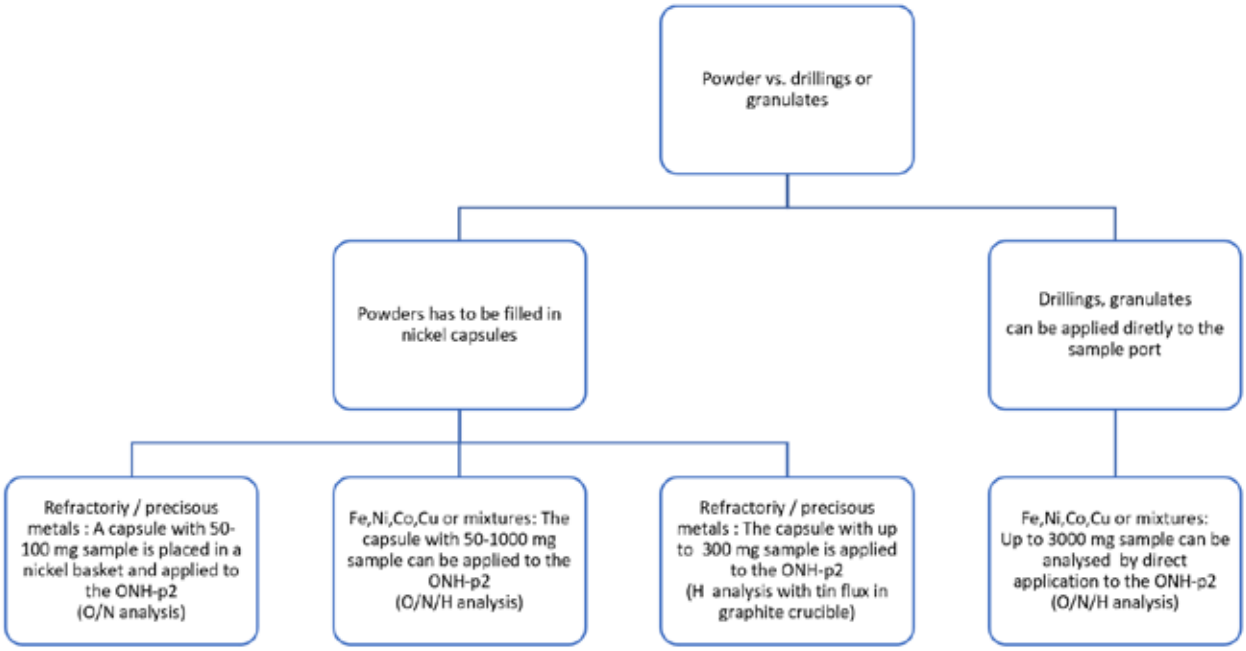


Figure 4: Application of a powdered sample in a nickel capsule

Figure 5: Application of accelerator to a crucible with sample

Figure 6: Application of a prepared sample to the CS-i analyzer

Usually, (battery component) samples which are subjected to an O/N/H analysis come in the shape of fine powders. These samples always require a nickel capsule before they can be applied to an elemental analyzer (Fig. 4). Without it they could cause blockages and the complete transfer to the graphite crucible would be unsafe.

Depending on the chemical nature of the powder, further sample preparation steps are required for a reliable oxygen and nitrogen analysis. Refractories and precious metals like titanium, palladium and platinum have a high melting point. To assure a complete release of the embedded gases additional flux needs to be provided. The nickel capsule with the high-melting sample is placed in an additional nickel basket to reduce the melting point of the resulting alloy in the crucible. For reliable analysis, the sample amount is usually limited to 50-100 mg for oxygen and nitrogen measurement.

Since hydrogen is released much easier from the sample in case of hydrogen analysis, the sample amount can be increased, and a nickel basket is not required. ELTRA recommends applying tin flux to the graphite crucible to assure a smooth release of the embedded hydrogen. The analysis of solid metal samples is limited to materials which are inert vs. atmospheric gases. The application of metal of e.g. lithium is not possible due to intensive reactions with atmospheric oxygen and water. Other not suitable samples for ON or H analysis comprise Lithium products like LiOH or LiS. These products react chemically with the upper electrode which impairs repeatability of measurements and causes maintenance issues.

Sample-related settings and preparation for CS analysis

In contrast to ONH analysis, less parameters have to be taken into account for a reliable CS measurement. The particle size distribution in general is negligible, but due to the intensive combustion, potential sample loss caused by swirling needs to be considered. With typical sample weights of 250 - 500 mg the sample is covered completely with accelerator and swirling is negligible (Fig. 5).

For higher sample weights the ELMENTRAC CS-i provides special solutions like induction power control and intelligent oxygen supply to ensure complete and smooth combustion without sample dust due to swirling or sputtering. Depending on the wide base of suitable samples, accelerators have to be added to guarantee a complete oxidation of the embedded carbon and sulfur. The following table summarizes typical sample weights and recommended accelerators:

Typical samples	**Recommended sample weight for C/S analysis (mg)**	**Recommended accelerator**
Iron, nickel, cobalt, lead	250-1000 mg	Tungsten (1.7g)
Copper	1000 mg	Copper (2g)
Metaloxides, carbonates, slags, refractories, precious metals	Up to 250 mg	Tungsten/Tin (2g); alternatively Iron (0.7g) + Tungsten (1.7 g)

Copper is printed in italic letters because the analysis of copper-based or copper-containing samples can be critical regarding precise and reliable sulfur analysis in general. Intensive combustion may cause minor sulfur determination induced by the forming of copper sulfide (ASTM E1941-10; Note 7).

A technical solution for this challenge is utilized in the ELEMENTRAC CS-i. A safe and reliable sulfur analysis in copper or even copper concentrates is enabled by the intelligent oxygen supply and ramping feature which allows for smooth combustion without forming of copper sulfide. For further information refer to ELTRA application notes 1037 and 1066.

Silicon nitride (CRM ED 101)

Application examples

In the following some typical applications for batteries are described in detail.

- O/N analysis of Si3N4 (ELTRA application note number 1099)
- C/S analysis of lead slag, carbonate and sulfate (ELTRA application note number 1100)

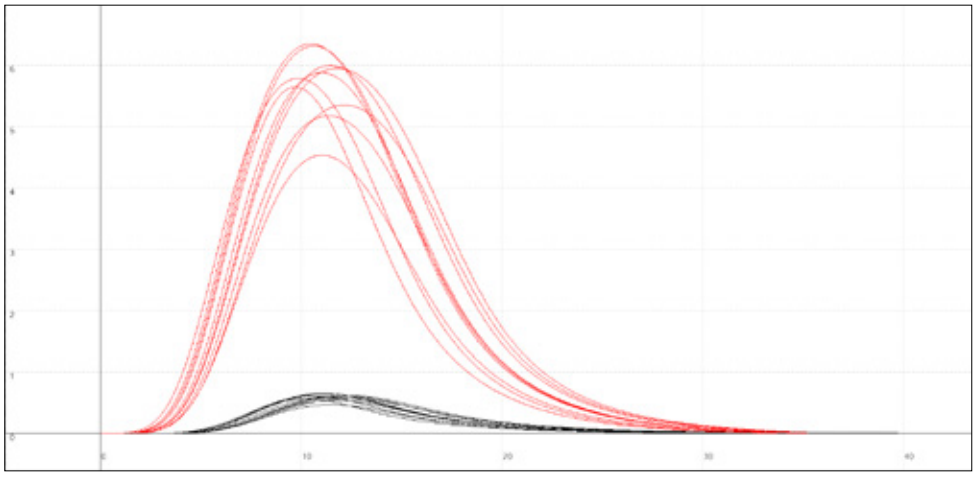
A) O/N analysis of silicon nitride (Si3N4)

Analysis	Oxygen and nitrogen with ELEMENTRAC ONH-p2
Sample	Silicon nitride ; Reference material CRM ED 101
Sample preparation	Sample was directly from the bottle, filled in nickel capsule
Settings	6000 W analysis power; carrier gas helium

Note

Lithium-based batteries can incorporate silicon nitride as part of an electrode. The nitrogen content is measured to indicate the purity of the silicon nitride, while the oxygen content is determined to evaluate electrical properties. The ELEMENTRAC ONH-p 2 is perfectly suited for precise measurements of both elements. The highly sensitive detectors used in ELTRA elemental analyzers accurately determine element concentrations ranging from low parts per million content to high percentages.

ERM – ED 101 (Silicon nitride)*		
Weight (mg)	**Oxygen (%)**	**Nitrogen (%)**
12.7	1.96	37.83
14.0	2.10	38.23
18.8	2.02	38.08
15.2	2.06	38.01
18.0	2.02	38.27
16.7	2.10	38.07
17.1	2.05	37.88
18.0	2.11	38.38
18.2	2.11	38.10
15.9	2.13	37.99
Mean value		
	2.07	38.08
Deviation / Relative deviation (%)		
	0.05 /2.6%	0.17/0.5 %
* Certified values: Oxygen (not certified); Nitrogen: 38.1% +-0.2		



Measuring graph
red peak: nitrogen signal black peak: oxygen signal
x-axis: time (sec) y-axis: intensity (voltage)

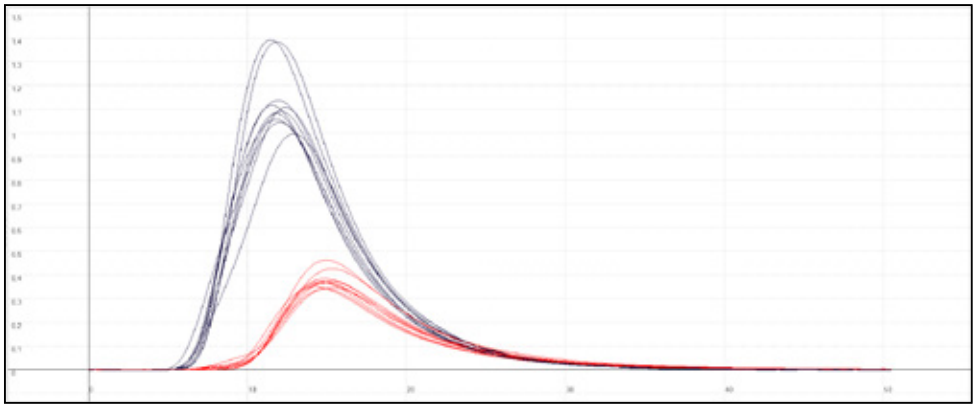
Silicon nitride (CRM ED 101)

B) Analysis from lead sulfate samples (customer samples from battery production)

Analysis	Carbon and sulfur with ELEMENTRAC CS-i
Sample	Lead sulfate from battery production
Sample preparation	Powder was applied as it is
Settings	Accelerator: Iron / Tungsten Analysis power: 90 % Generator time 40 sec Gas flow chamber: 5 sec Gas flow chamber/lance: 5 sec

Note
Sulfur measurement by combustion analysis is used for final quality control of charged lead-based batteries. The electrodes consist of lead and lead oxide and need to be free of sulfur. The properties of the battery paste have an impact on the performance and life span of the battery and the contained lead sulfate determines its qualities. ELTRA's C/S analyzers provide rapid and reliable measurement of carbon and sulfur concentration from the low ppm range up to 100%

Lead sulfate (customer sample from battery production)		
Weight (mg)	**Carbon (%)**	**Sulfur (%)**
70.4	0.139	5.60
71.8	0.163	5.91
70.0	0.138	5.64
70.9	0.140	5.52
76.9	0.163	5.85
73.4	0.152	5.62
71.8	0.162	6.15
89.3	0.144	5.81
66.9	0.146	5.62
71.0	0.136	6.07
Average values		
	0.148	5.78
Deviation / Relative deviation (%)		
	0.01 (7.4%)	0.21 (3.8%)



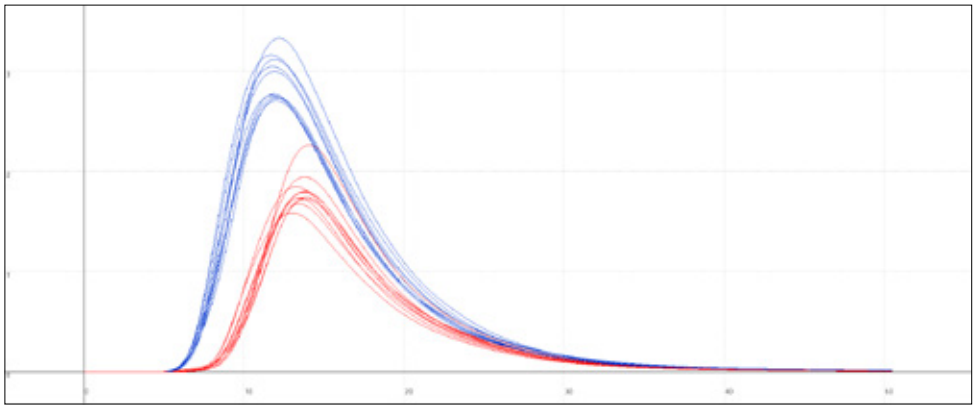
Measuring graph
red peak: sulfur signal
x-axis: time (sec)
black peak: carbon signal
y-axis: intensity (voltage)

Lead carbonate (customer sample from battery production)

C) Analysis from lead carbonate samples (customer samples from battery production)

Analysis	Carbon and sulfur with ELEMENTRAC CS-i
Sample	Lead carbonate from battery production
Sample preparation	Powder was applied as it is
Settings	Accelerator: Iron / Tungsten Analysis power: 90 % Generator time 40 sec Gas flow chamber: 5 sec Gas flow chamber/lance: 5 sec

Lead carbonate (customer sample from battery production)		
Weight (mg)	**Carbon (%)**	**Sulfur (%)**
68.6	3.17	1.23
74.6	3.21	1.13
69.9	3.34	1.13
72.1	3.23	1.06
75.4	3.36	1.20
72.6	3.21	1.14
92.8	3.13	1.15
68.3	3.29	1.17
89.8	3.22	1.12
72.3	3.20	1.17
Average values		
	3.23	1.15
Deviation / Relative deviation (%)		
	0.069 (2.1%)	0.046 (4%)



Measuring graph
red peak: sulfur signal
x-axis: time (sec)

blue peak: carbon signal
y-axis: intensity (voltage)

Lead slag (customer samples form battery production)

D) Analysis from lead slag samples (customer samples from battery production)

Analysis	Carbon and sulfur with ELEMENTRAC CS-i
Sample	Lead slag from battery production
Sample preparation	Powder was applied as it is
Settings	Accelerator: Iron / Tungsten Analysis power: 90 % Generator time 40 sec Gas flow chamber: 5 sec Gas flow chamber/lance: 5 sec

Note
The lead content of batteries can be recycled for use in new batteries in an environmentally friendly way. Lead is present as lead sulfate in exhausted batteries, and also in slags which are a byproduct of battery production and recycling. Sulfate can be precisely measured using ELTRA's C/S combustion analyzers, allowing fast and easy determination of the present lead. Lead slag is a very heterogeneous sample. Whereas the other lead samples could be measured within a reliable repeatability, the precision for carbon and sulfur measurements in slag is low. Nevertheless, it is possible to use this application for the C/S determination in slag and get an overview about its carbon and sulfur content. Due to the large deviation, an RSD and average was not calculated. The repeatability could be improved by the utilization of a laboratory ball mill for sample homogenization, but safety of the laboratory staff has to be considered.

Lead slag (customer sample from battery production)		
Weight (mg)	**Carbon (%)**	**Sulfur (%)**
72.8	4.5	7.7
58.4	8.7	13.4
60.2	9.4	13.1
62.5	7.0	12.3
61.3	14.3	11.3
69.0	16.5	11.1
68.6	9.8	8.9
53.1	8.6	9.9
64.9	8.1	12.7
72.0	9.9	8.8