

Direct solid sample analysis of artificial slags by ETV-ICP-OES

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INTRODUCTION

The analytics of slags from lithium-ion battery (LIB) recycling processes are highly relevant in a circular economy. For research purposes artificial slags closely related to recycling slags are surveyed.

The release behaviour of relevant elements, especially Lithium (Li) and Manganese (Mn), is researched with direct solid analysis by electrothermal vaporisation (ETV) coupled to an atomic emission spectrometer with inductively coupled plasma (ICP-OES). The solid sample is heated inside a graphite furnace, vaporized, and introduced into the ICP-OES. Halogenated reaction gas can be used for a more defined element release. Measurements with and without reaction gas were conducted to study element release from the slag at high temperatures. Additional, different heating rates and holding times are surveyed.

ARTIFICIAL RECYCLING SLAG

End-of-life LIBs are recycled in a combination of pyro- and hydrometallurgical processes. Particularly the recovery of Li in the presence of Mn in pyrometallurgical processing is quite challenging [1]. While most metals from the LIB cathodes are recovered directly or as alloys, Li passes into the slag, resulting in lower recovery yields [2,3]. Conventional pyrometallurgical extraction routes resulting in about 74.3 % of the Li in the slag and due to its volatile behaviour 25.4 % Li in the flue dust [4,5]. Hydrometallurgical process routes are reported with up to 30 % Li loss [3].

The modification of slag phases by concentrating target elements into preferred phases is a strategy for higher recovery rates. In the formation of these Li-enriched engineered artificial minerals (EnAM) Mn has a suppressing influence, spinels and spinel solid solutions have been reported [1,6]. The increasing quota of Mn-containing LIB cathodes commends further research on Mn-containing slag systems [7].

Artificial recycling slags are used for systematic development of new recycling processes and routines [7]. Based on the UMICORE *High Manganese (High Mn)* slag [1] an artificial slag from Al₂O₃, SiO₂, CaO, MgO, MnO, Li₂O/Li₂CO₃ was formed under reductive conditions, resulting in different oxidation states of Mn in this slag.

MEASUREMENTS WITH AND WITHOUT REACTION GAS

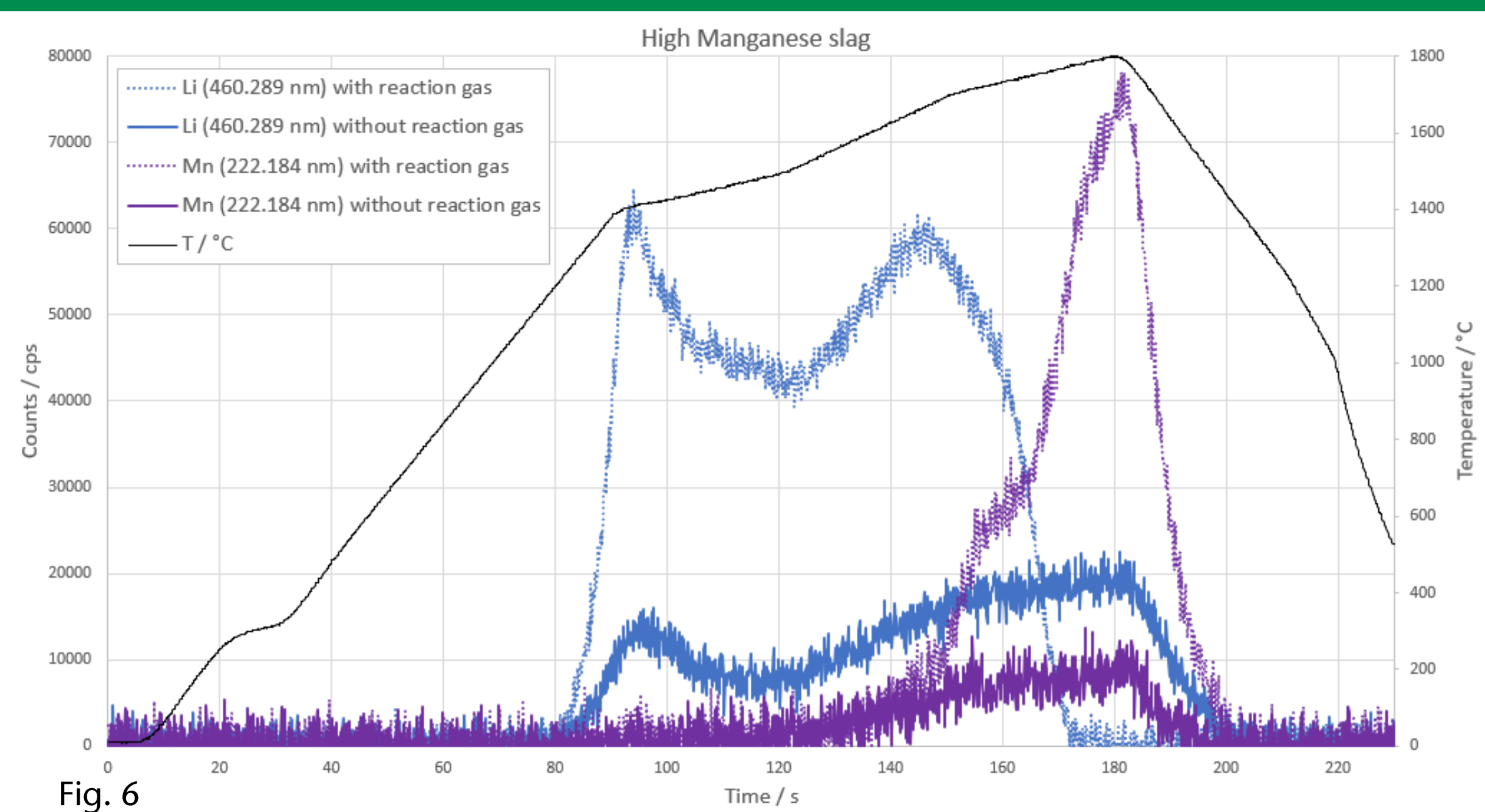


Fig. 6

Depending on the elements and their likelihood of carbide forming with the ETV graphite boat and furnace, different volatile behaviour is described [9]. ETV measurements without reaction gas (only with Argon as transport gas) allow the comparison of the volatile Li with the other analytes. For a complete vaporisation and a simultaneous Li analysis of all analytes, the use of reaction gas is recommended. The difference of the use of reaction gas is shown in Fig. 7 and 8.

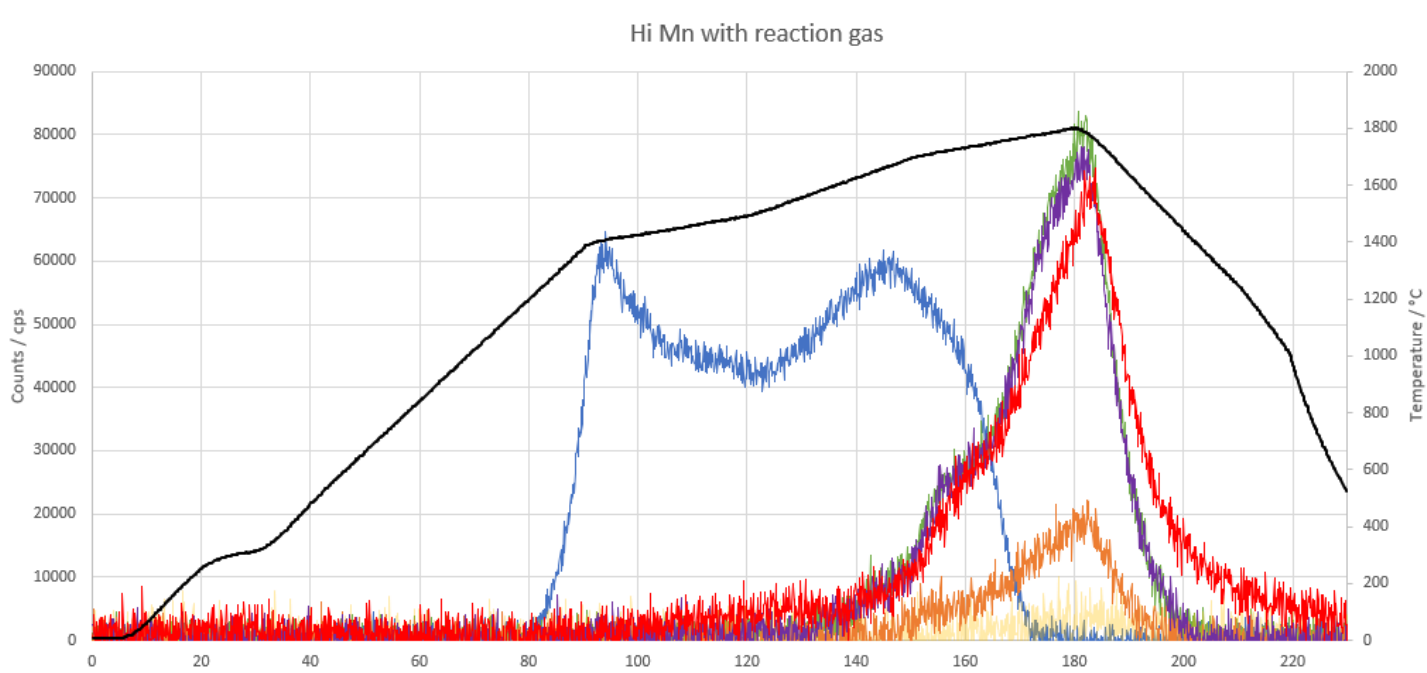


Fig. 7

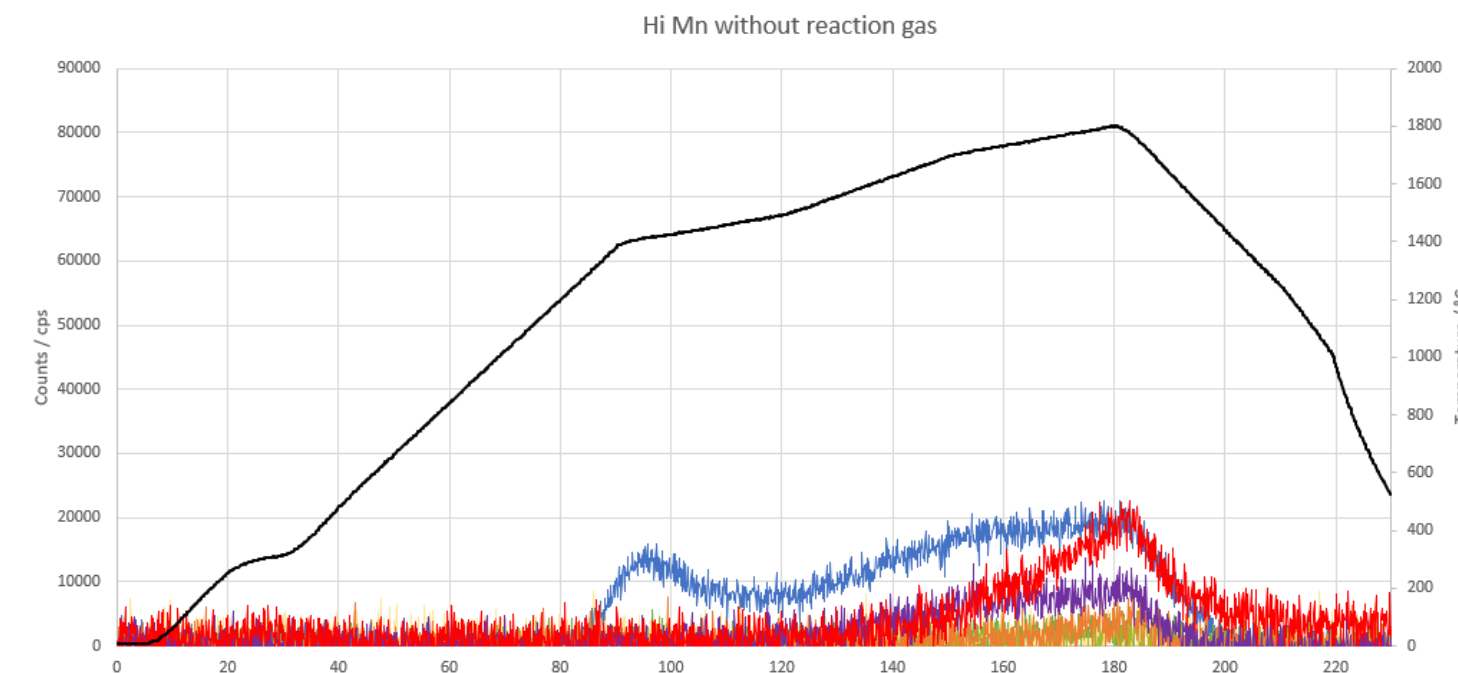


Fig. 8

CONCLUSION & OUTLOOK

ETV-ICP-OES measurements allow conclusions about the compounds and phases of the investigated slag due to the temperature dependency of the recorded elemental release.

Further optimisation of the ETV temperature profile for clearly separated elemental release peaks will be investigated. Comparative measurements with reference materials for speciation are mandatory. Thereby trials for elemental quantification of main elements in slag matrices are ongoing.

The slag phase analyses will be assisted by X-ray absorption near edge spectroscopy (XANES), powder X-ray diffraction (PXRD), and electron probe microanalysis (EPMA) measurements. In continuation, the comparison with known slag phases will be carried out.

Acknowledgments:

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INSTRUMENTATION



Mörtenkötter, H.; Grünwald, D.; Fendt, S.; Spliethoff, H. *Waste Biomass Valor* **2023**, doi:10.1007/s12649-023-02129-0

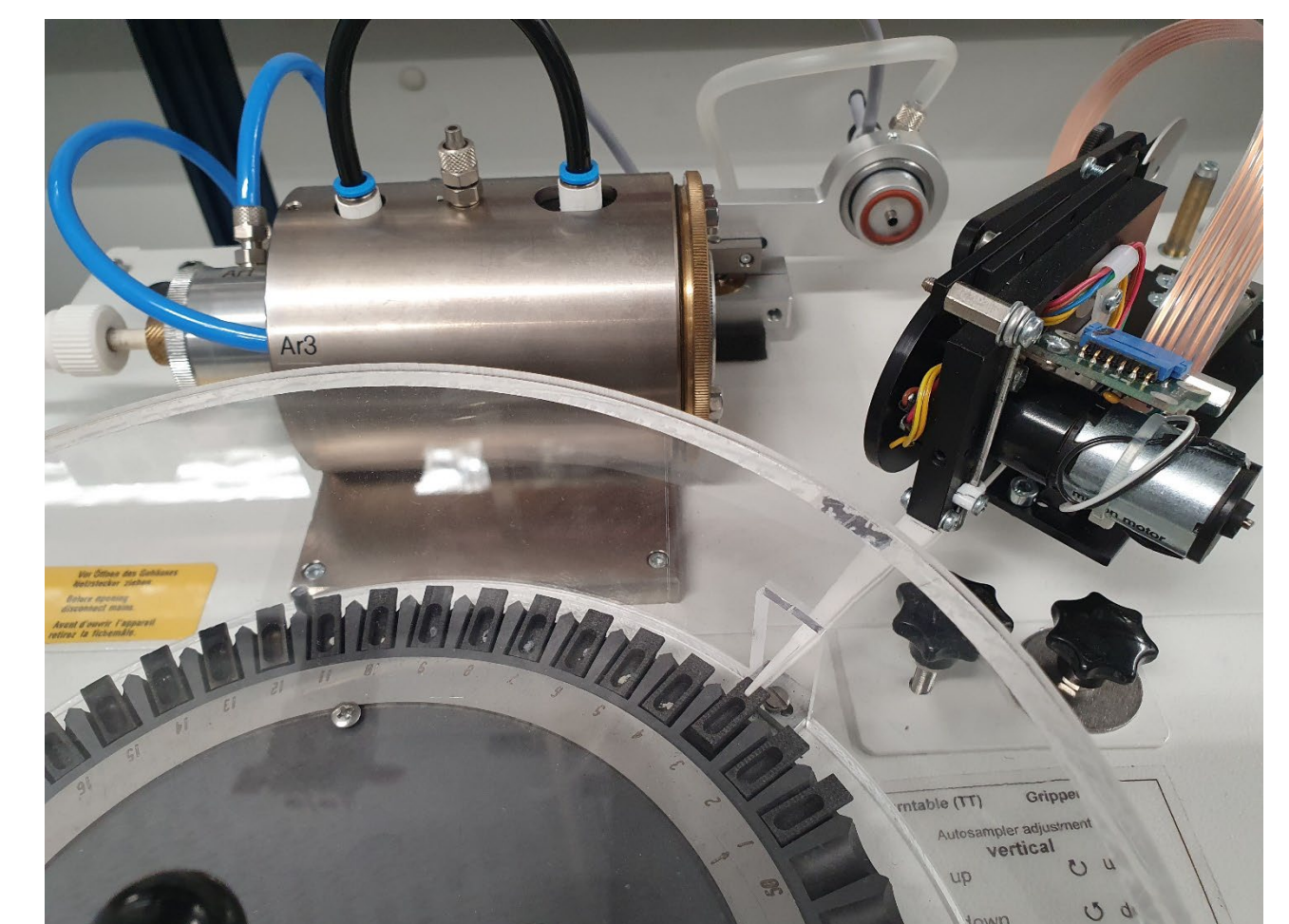


Fig. 2: ETV 4000d furnace with loaded autosampler

Fig. 1: ETV schematic, taken from [8]

- ETV 4000d with Autosampler AD-50-III (SPECTRAL SYSTEMS) electrical heated graphite furnace for temperature-controlled evaporation of solid samples with a temperature range from room temperature to 2500 °C and definable heating rates. Vaporised elements and compounds are introduced into the plasma of the ICP-OES as a dry aerosol via Argon transport gas.
- ARCOS II MV 130 (SPECTRO ANALYTICAL INSTRUMENTS) ICP-OES with simultaneous spectrum capture in the 130-770 nm wavelength range and interchangeable axial/radial-view optical MultiView interface.
- Tetrafluoromethane CF₄, Freon R 14, is added into the transport gas of the ETV as reaction gas / modifier. It converts hardly volatile elements or carbide-forming elements into low-boiling halogen compounds.

EXPERIMENTAL

- The fine milled artificial slag is weighed into the graphite sample boat (Fig. 3) with sample masses about 1 mg.
- Temperature programs with definable heating rates and times are deployed.
- Signals are recorded time-resolved at 10 Hz by the ICP-OES.
- The time-resolved recording enables temperature-dependent release behaviour to be recorded.

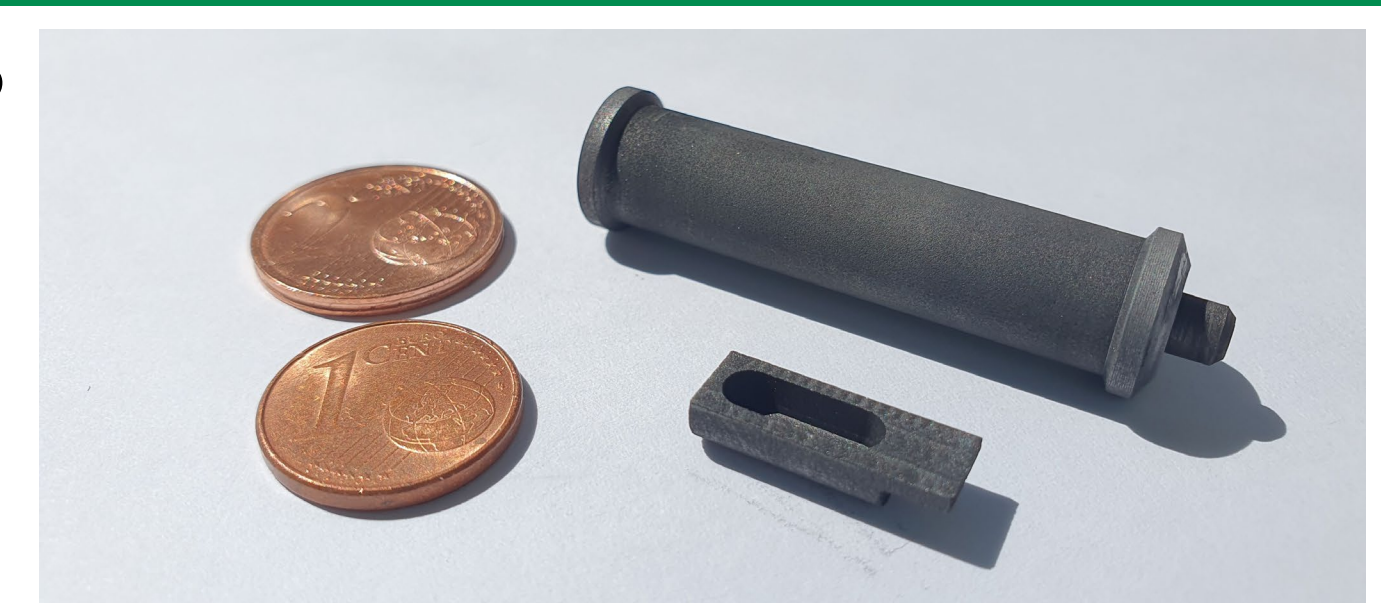


Fig. 3: standard ETV graphite furnace and graphite sample boat next to 1 and 2 Euro coins

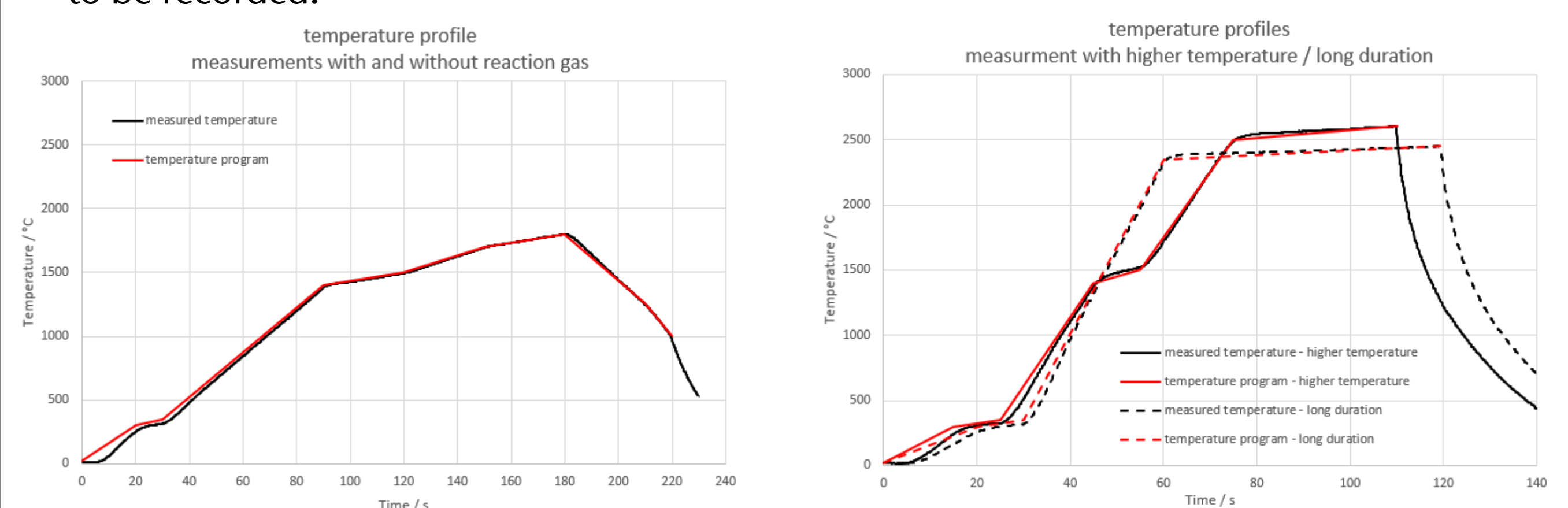


Fig. 4 + 5: temperature programs and measured temperature profiles

MEASUREMENTS WITH DIFFERENT TEMPERATURE PROFILES

The release behaviour of an element at different temperatures during one measurement can indicate the presence of different compounds and possibly deviating oxidation states of said element. Characterisation and speciation of elements via ETV-ICP-OES are known from literature [10].

During method development the maximum temperature, heating rates and durations, and holding times are varied, the element release behaviour changes.

Increased duration allows a complete release of relevant elements (Fig.9).

Most prominent for Mn and Mg in Fig. 10, lower heating rates show additional defined element release peaks. With higher heating rates those peaks are enlaced in the main peak (Fig.9).

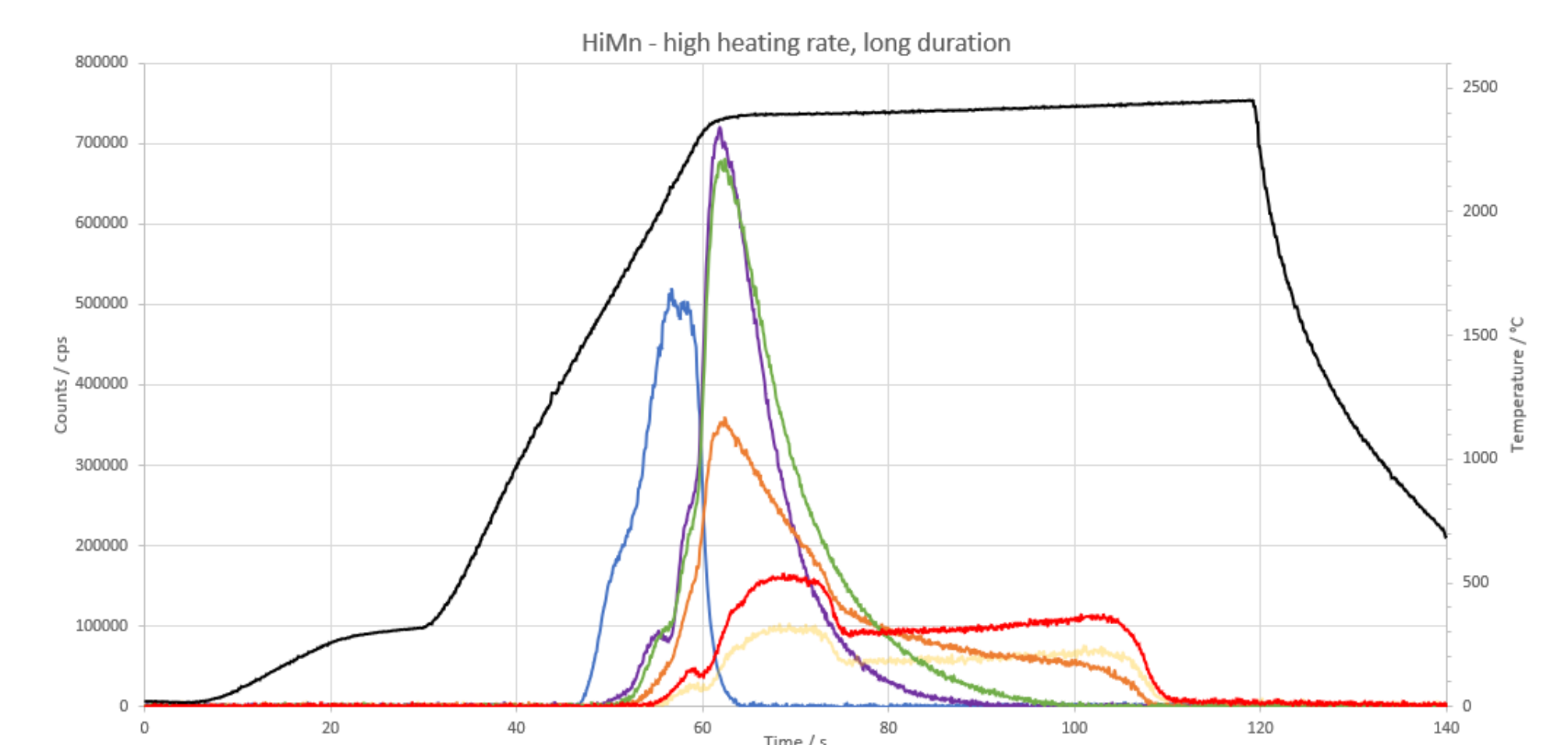


Fig. 9

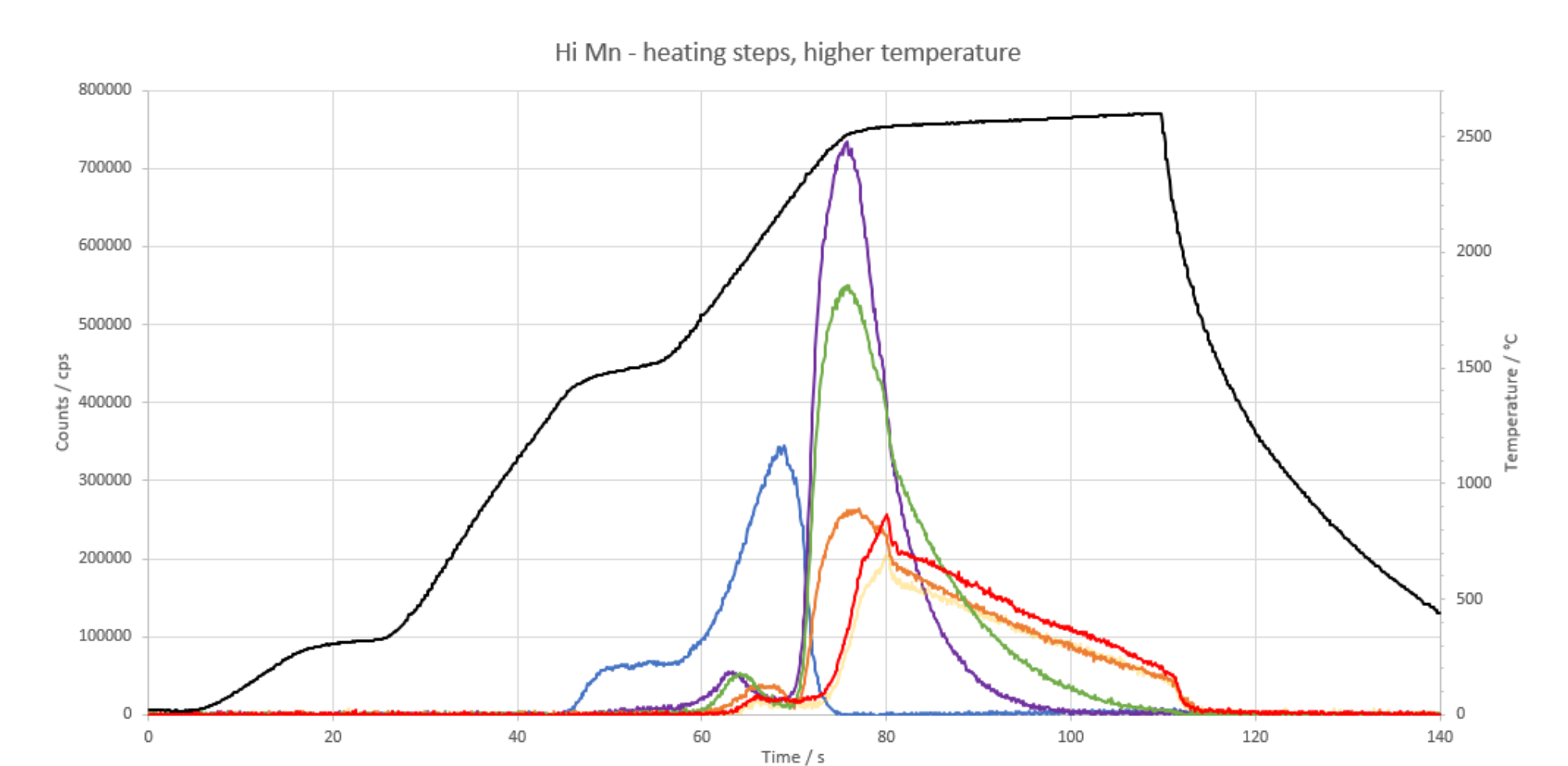


Fig. 10

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