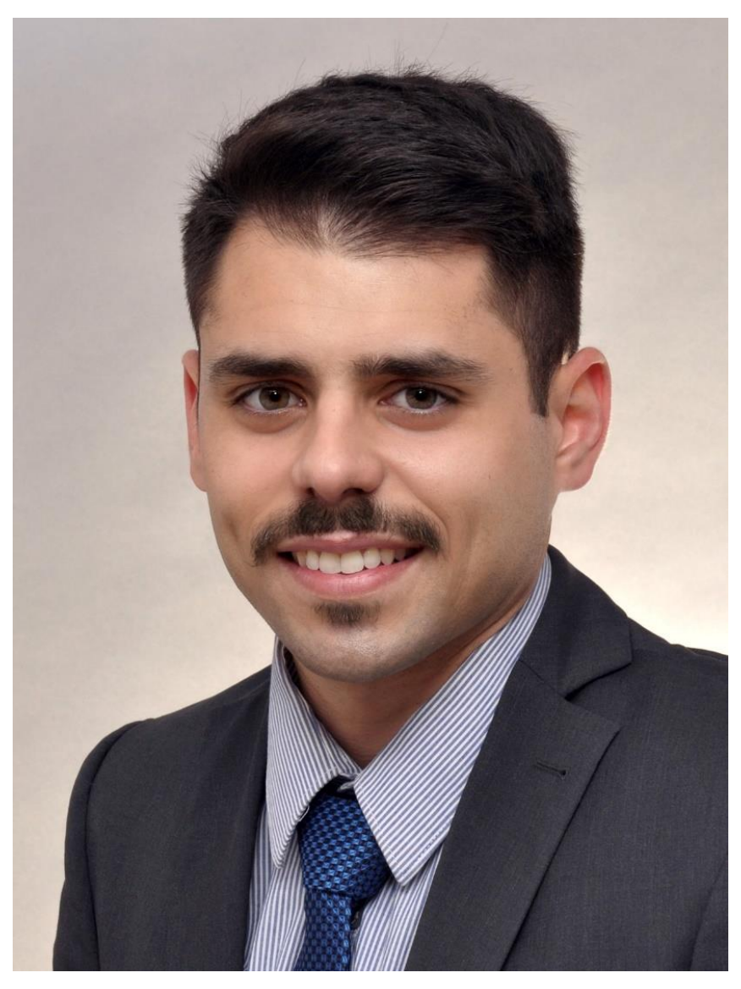
European Metallurgical Conference 2025

A new Photometric Protocol for Analyzing of the Iron Oxidation State in Fayalitic Slag Systems

Monika Keutmann
Dipl.-Ing. Joao Weiss
Prof. Bernd Friedrich

IME - Process Metallurgy
and Metal Recycling
Institute and chair at
RWTH Aachen University



Introduction

Iron has three typical oxidation states Fe(0), Fe(II) and Fe(III). As metal it has an oxidation state of 0. The most common mineral of iron is Hematite, where the oxidation state is III. In metallurgy a typical slag system is Fayalitic slag system, here the oxidation state is II. So the oxidation state of iron provides an indication of the micro structure of a mineral system.

Theoretical Background

For recycling of Tantalum from e-waste a new approach should be investigatet. Here the main goal is to enrich Tantalum in a specific mineral phase like ($Fe^{II}(Fe^{III}_{(2-5/3x)}Ta_x)O_4$). As a starting point a synthetic Fayalitic slag system was used. So the oxidation state of iron is able to indicate indirectly information of Tantalum phases.[3] Therefore a special protocol for Analyzing iron with a photometric method was investigatet.

Experimental

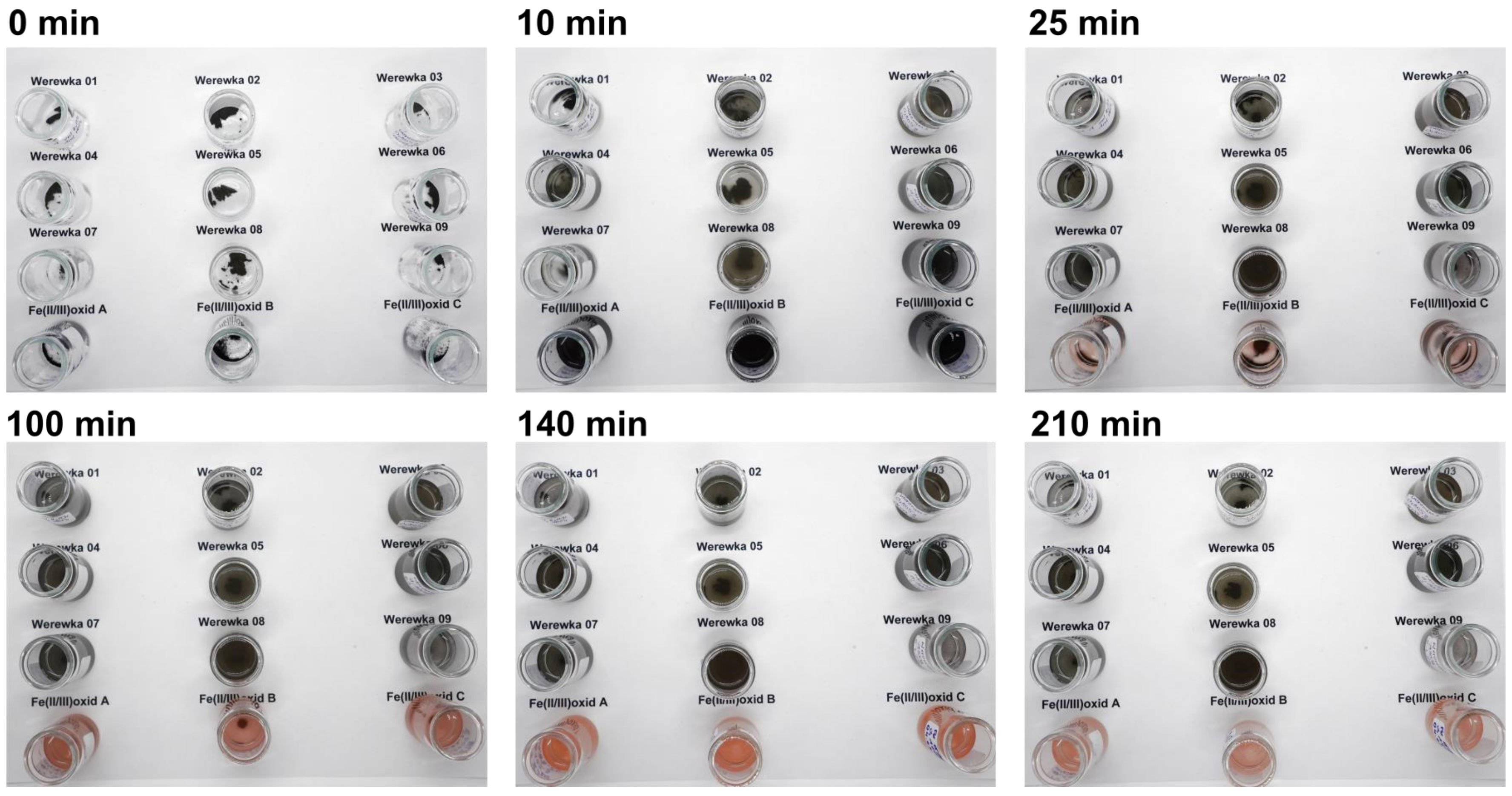


Figure 1: Dissolving behavior of slag samples and iron oxide in relation to the time

First the slag has to be dissolved without changing oxidation state of iron. As reference pure Iron(II/IIII)oxide (FeO/Fe_2O_3) from Sigma was used. A mixture of ortho phosphoric acid (H_3PO_4), Tetrafluoroboric acid (HBF_4) and water (H2O) was used. As shown in figure 1 the iron oxide, it's the bottom line with three samples, dissolved completely after 140 min. The slags are not completely dissolved after 210 min. So an ultra sonic bath was used. Here most of the samples were successful dissolved. The rest could be silicon dioxide (SiO_2), which is quite hard to dissolve. The samples were each transferred quantitatively with water to a 500 mL volumetric flask, the flask is filled to the mark and its contents are mixed. Afterwards the solution are diluted again for factor of 50. In these study two different photometric kits from Merck were used for the photometric determination. **Test kit 1** was Cat. No, 1.14761.0001 Spectroquant® with a triazine derivate as complex builder. An assumed reaction[1] and color of an sample see figure 2. **Test kit 2** was Cat. No, 1.00796.0001 Spectroquant® with a 1,10-phemanthroline as complex builder. The reaction of Fe(II) and Fe(III) ions[2] and color of the Fe(II) complex is illustrated in figure 3.

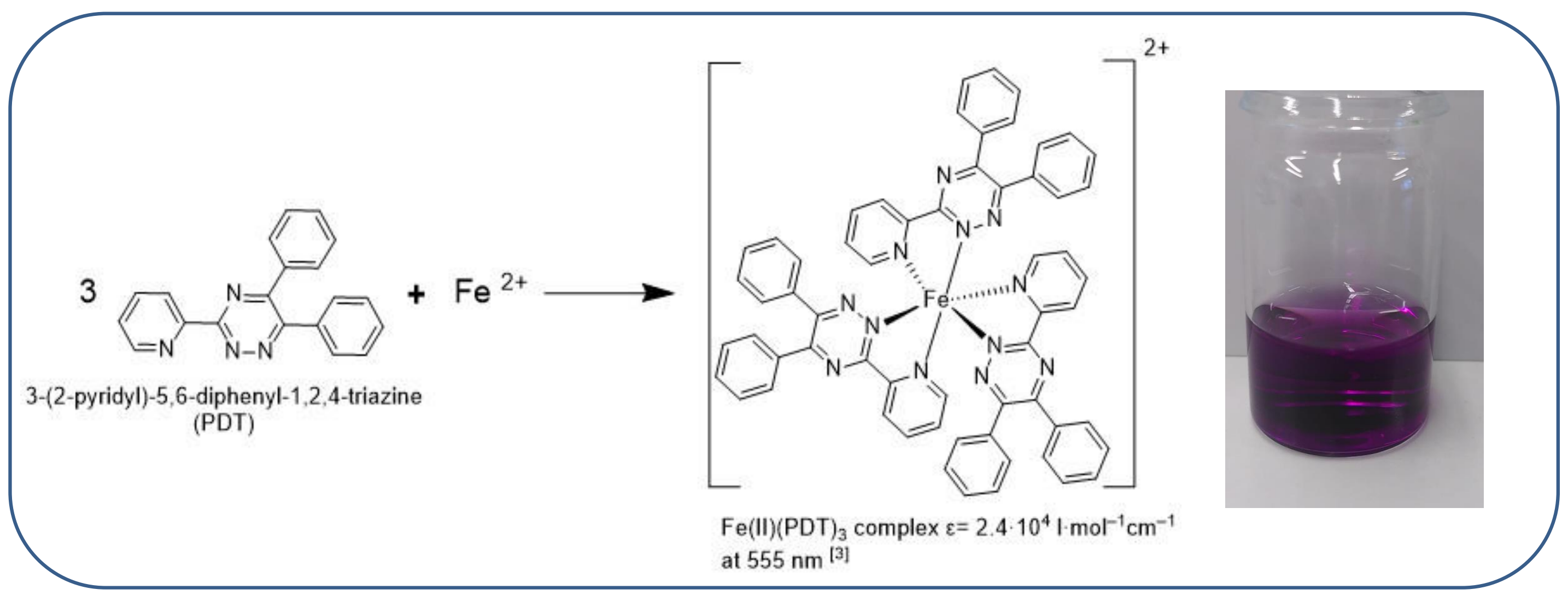


Figure 2: Test kit 1. Right side, assumed reaction of Fe(II) and a triazine derivate as complex builder [1]. Left side a positive sample with test kit 1

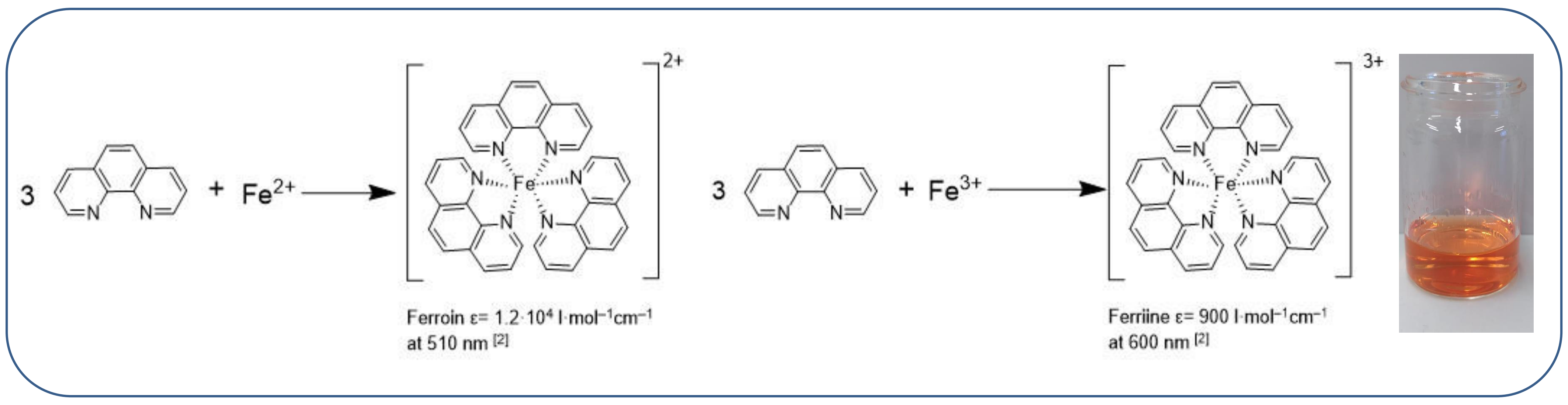


Figure 3: Test kit 2. Right side, reaction of Fe(II) and 1,10-phemanthroline as complex builder[2}. Middle, reaction of Fe(III) and 1,10-phemanthroline as complex builder[2} Left side a positive sample with test kit 1 with Fe(II).

Results and Discussion

For comparing the test kits, iron oxide samples were measured with both test kits. Test Kit 1 always reduce all Fe-Ions to the oxidation state of II, while in test Kit 2, it is possible to measure Fe(II) separately from Fe(III). Here the difference between both Kits was overall ± 5% in total iron amount. So both Kits are comparable. The ratio of Fe(II) and Fe(III) of the samples were close to results from X-ray absorption near-edge structure (XANES) spectroscopy compared to Schimrer et.al[3].Now some confusion results were detected. The total amount is too high. The results from iron oxide samples were calculated back into a weight and with initial weight of the sample. Here the recovery Rate of 168 % ± 5% were calculated. Therefore, the method of Standard addition was used, allowing to detect matrix effects. Three different calibration curves are reflected in figures 4-6. The results indicate clearly that the matrix has to be consider for detecting the correct concentration. So for future calculation, curves with standard addition should be used.

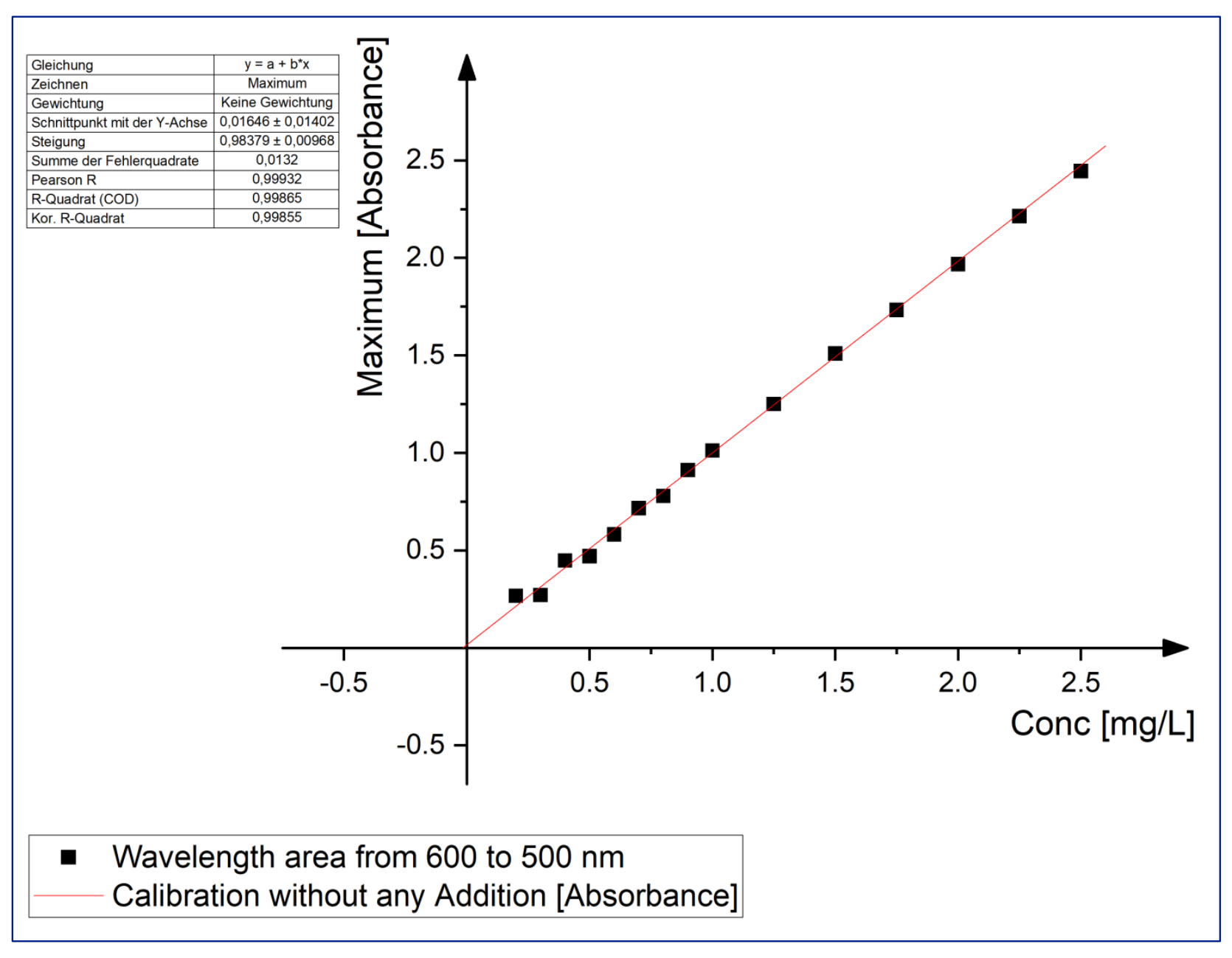


Figure 4: Calibration Curve with test Kit 1 without any matrix.

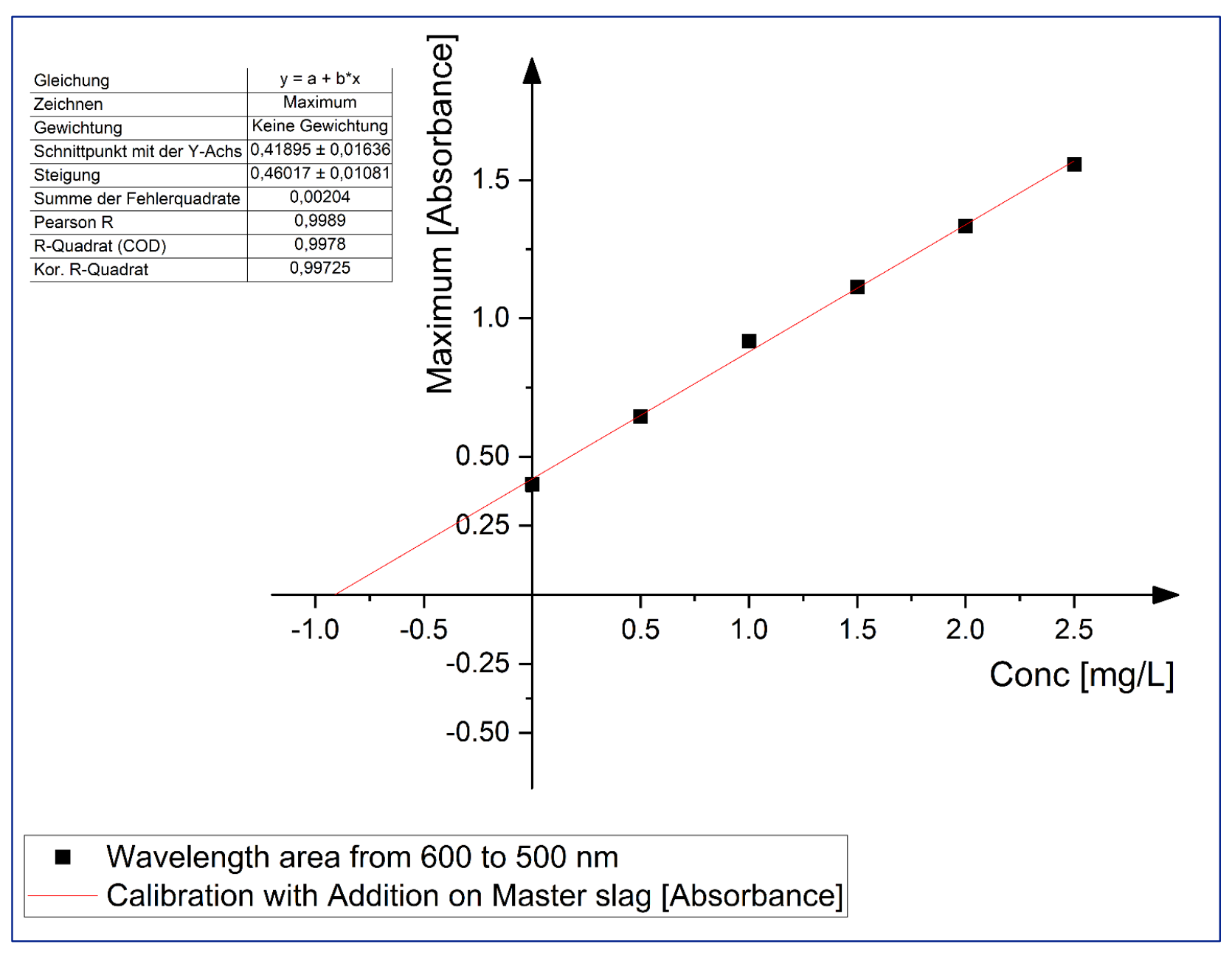


Figure 5: Calibration Curve with test Kit 1 with slag matrix.

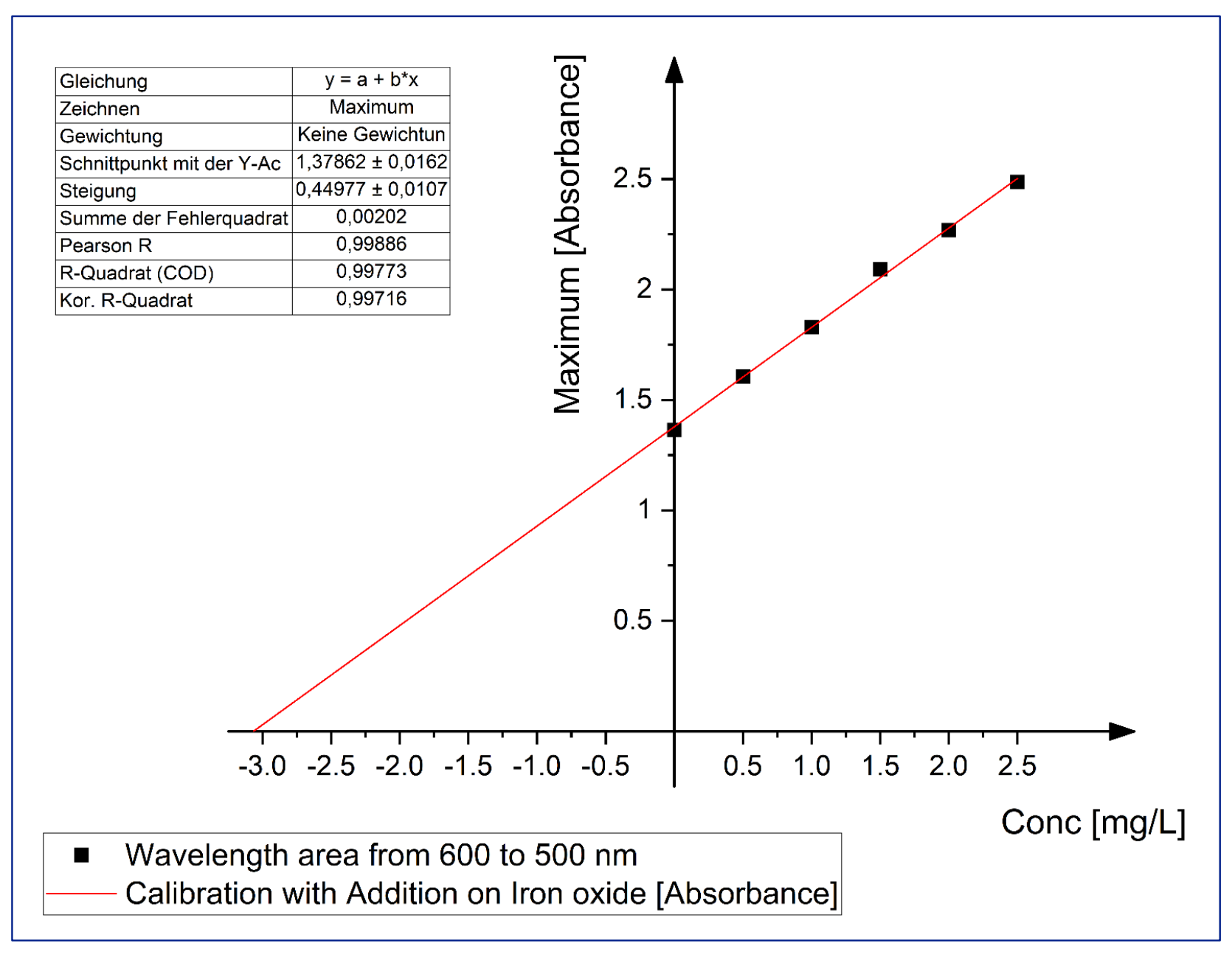


Figure 6: Calibration Curve with test Kit 1 with iron oxide matrix.

Litrature

[1] Croot, P.L.; Hunter, K.A. Determination of Fe(II) and total iron in natural waters with 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine (PDT). *Analytica Chimica Acta* **2000**, *406*, 289–302, doi:10.1016/S0003-2670(99)00758-8.
[2] Oslonovitch, J. Untersuchungen zum Mechanismus der Ferroin-katalysierten Belousov-Zhabotinsky-Reaktion; Philipps-Universität Marburg, Marburg, **1997**.
[3] Schirmer, T.; Hiller, J.; Weiss, J.; Munchen, D.; Lucas, H.; Fittschen, U.E.A.; Friedrich, B. Behavior of Tantalum in a Fe-Dominated Synthetic Fayalitic Slag System—Phase Analysis and Incorporation. *Minerals* **2024**, *14*, 262, doi:10.3390/min14030262

GESELLSCHAFT DER METALLURGEN UND BERGLEUTE E.V.
PAUL-ERNST-STRAßE 10, 38678 CLAUSTHAL-ZELLERFELD
CONTACT | PHONE.: +49(0) 5323 9370 | EMAIL: GDMB@GDMB.DE