Automated potassium pyrosulfate fusion for X-ray fluorescence analysis

Abstract

In this application note, we present the performance of an automated potassium pyrosulfate ($K_2O_7S_2$) fusion system that enables a matrix-independent XRF analysis of various samples types. The system covers fusion, casting of the melt and the subsequent preparation of a pressed pellet suitable for XRF analysis. In a test series of nine identical samples the relative standard deviation of the concentration of the major matrix elements was 0.5 % or less. This demonstrates the high analytical reproducibility of the system. Moreover, in a further series with intermittent preparation of blank samples we found no indication for cross-contamination between subsequent samples.

Key words

• **Potassium Pyrosulfate** • **Fusion** • **Grinding** • **Pressing** • **Automation** • **XRF**

Introduction

Here we describe a robot system for sample preparation by means of fusion with potassium pyrosulfate ($K_2O_7S_2$) in a silica crucible. Following fusion and cooling down of the melt, the material is fully-automatically ground, pelletized in a 51.5 mm steel ring and analyzed by X-ray fluorescence spectroscopy (XRF). Typical applications for this technology are preparation of copper, copper alloys, lead, mattes, ferroalloys, slags, iron ores and recyclates containing non-ferrous and precious metals. Because of its easy operation and cost-effectiveness the pyrosulfate technology is regarded as an alternative to the frequently used borate fusion.

In this study, we aimed at determining the reproducibility of the automated system by assessing the variability of the chemical composition in a test series of nine subsequent samples. Furthermore, we investigated the effectiveness in preventing cross-contamination between successive samples with widely differing element concentrations.

Methods

The automated system consists of a robot cell which is connected to an automatic mill and press (Figure 1). To begin with, the operator inserts a boro-silicate/quartz crucible with the pre-weighted sample and flux into the input magazine of the automation. Usually, the ratio

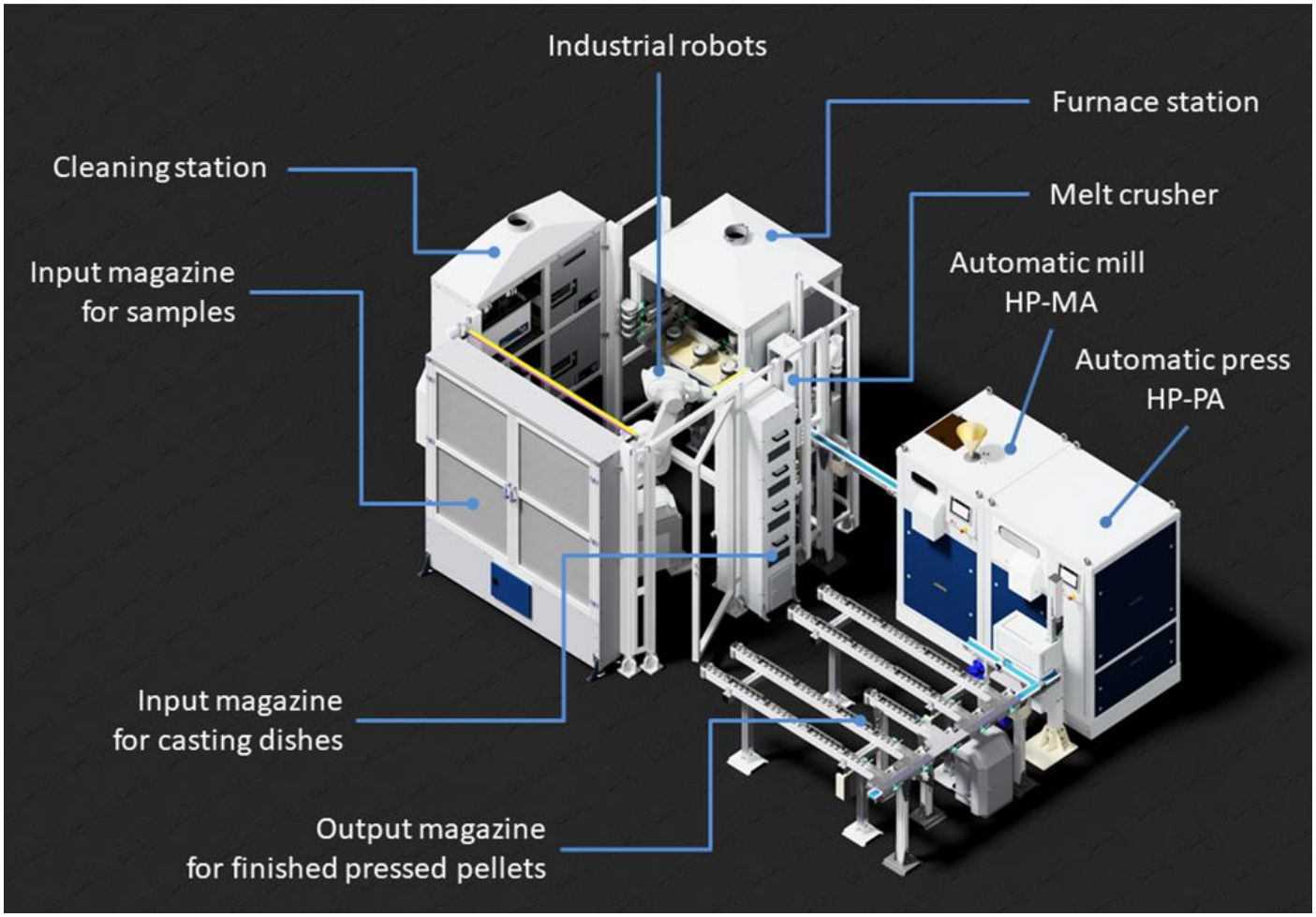

Figure 1: *Layout of the automated system for pyrosulfate fusion, crushing, pulverizing and pelletizing of sample material. A further component of the automation is the cleaning station for ultrasonic cleaning and hot air drying of the crucibles containing solidified rest material after fusion.*

between fine powered sample and flux varies between 1:10 and 1:25. Following registration of the sample the industrial robots moves the crucible to the furnace station. The crucible is loaded into the furnace from below in order to ensure minimum temperature loss and efficient fume removal. The heating elements are protected by an isolating tube in the furnace. Depending on application and sample type the fusion usually takes place at a temperature between 500°C to 1000°C. As soon as the fusion is completed the melt is quickly poured into a special casting dish by the robot (Figures 2 and 3). All processes are optimized and timed to ensure complete discharge of the crucible and to minimize the sample residue.

The sample is then comminuted by a roller crusher specially designed to avoid contamination and allow efficient automatic cleaning of its surface. The sample granulate is collected in a cup and passed on via a conveyor belt to the automatic vibrating disk mill type HP-MA for fine grinding. The ground material is subsequently pelletized into a standard 51.5 mm steel ring by the HP-PA tablet press and is then available for spectrometric analysis.

The automation unit is controlled by the PrepMaster Scada system. The software allows easy registration and tracking of samples. All relevant parameters for system control can be changed by an authorized user from the PrepMaster workstation. At the same time, PM Core establishes a connection to superordinate host systems for exchanging and processing important data such as ident information.

In order to determine the reproducibility, we performed nine subsequent trials with preparation of samples from the same material. In each trial we used identical preparation parameters for fusion, grinding and pelletizing. Then we analyzed the pressed pellets by means

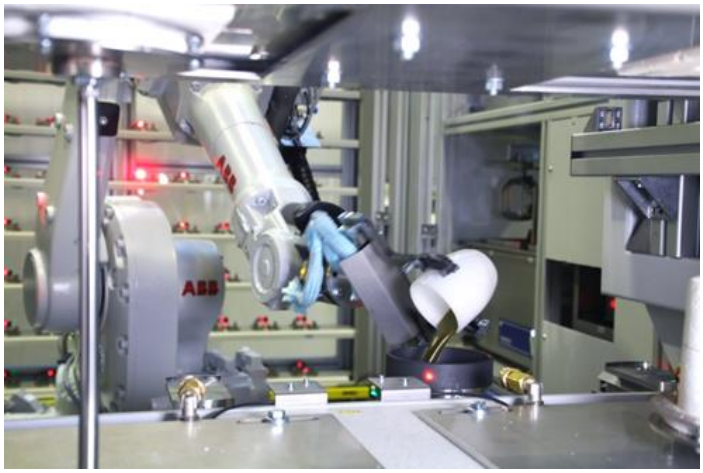

Figure 2: *Pouring of the melt from the crucible into the casting dish by the multi-axis robot .*

Figure 3: *Casting dishes are designed to allow quick cooling and prevent sticking to the wall.*

of XRF (Epsilon 3XL) and calculated the mean average, standard deviation and relative standard deviation of the main elements contained in the sample.

For investigation of cross-contamination we performed a test series of eleven subsequent trials where one sample was followed by two blanks consisting of pure potassium pyrosulfate. To detect a possible carry-over from the sample into the blank we assessed the counting rates of the spectrometric measurement for each trial. Furthermore, two samples were prepared manually in order to exclude a systematic effect originating from the automatic system.

Results

The first test series of nine subsequent samples revealed a high degree of analytical reproducibility. In all elements but Sb the relative standard deviation was below 1.0 %. Cu, Pb and Fe were the elements with the highest fraction in the sample. For these elements the relative standard deviation was 0.42 %, 0.53 % and 0.46 % (Table 1). Only Sb showed a slightly higher standard deviation with 1.61 % whereas the total amount of this element was relatively low with 0.52 %.

The second test series with the alternating preparation of sample and blank showed no evidence for cross-contamination. Accordingly, the elemental counting rates for blanks prepared after a sample were in the same range as the background activity found in the blanks which were prepared manually (red bars, Figure 4). Furthermore, the counting rates were equal to or lower than for the blank examined at the beginning of the test series.

	Cu (%)	Pb (%)	Fe (%)	Zn (%)	Ni (%)	Sn (%)	Sb (%)	As (%)	Co (%)
Sample 1	27.37	25.67	17.20	2.02	1.79	1.47	0.51	0.45	0.22
Sample 2	27.37	26.11	17.25	2.02	1.80	1.48	0.53	0.45	0.22
Sample 3	27.36	25.86	17.17	2.02	1.79	1.47	0.51	0.46	0.22
Sample 4	27.46	25.96	17.28	2.03	1.79	1.46	0.51	0.45	0.22
Sample 5	27.11	25.77	17.05	2.00	1.77	1.48	0.53	0.45	0.22
Sample 6	27.48	25.85	17.31	2.02	1.82	1.48	0.52	0.46	0.22
Sample 7	27.43	25.95	17.21	2.03	1.79	1.47	0.52	0.45	0.22
Sample 8	27.37	26.02	17.27	2.03	1.79	1.47	0.52	0.45	0.22
Sample 9	27.49	25.79	17.28	2.02	1.80	1.48	0.51	0.45	0.22
Mean	**27.38**	**25.89**	**17.22**	**2.02**	**1.79**	**1.47**	**0.52**	**0.45**	**0.22**
SD	**0.11**	**0.14**	**0.08**	**0.01**	**0.01**	**0.01**	**0.01**	**0.00**	**0.00**
Relative SD	**0.42**	**0.53**	**0.46**	**0.46**	**0.74**	**0.48**	**1.61**	**0.98**	**0.00**

Table 1: *Individual results of the element concentration from the test series with nine samples of the same material. Additionally, the mean average, standard deviation (SD) and relative standard deviation (relative SD) are displayed.*

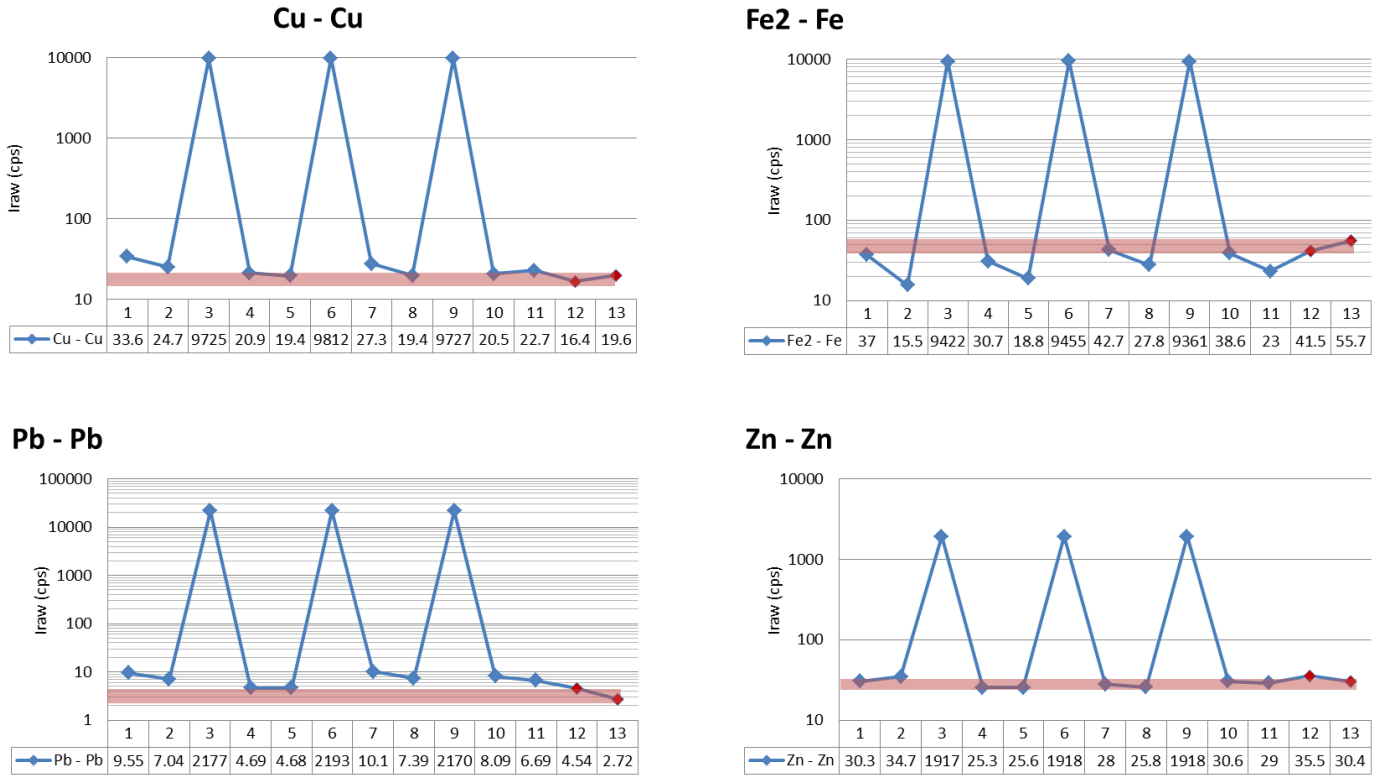

Figure 4: *Counting rates (cps) of samples (trials 3, 6, 9) that were alternately prepared with blanks. Red dots (trials 12, 13) represents blanks prepared manually, the red bar the expected background activity of blanks for each element.*

Discussion

The results of this study clearly demonstrate that the automated pyrosulfate fusion system allows a reproducible sample preparation and precise XRF analysis. This implies that all processes are optimized to guarantee perfect operating conditions for each preparation step and to minimize material loss. For example, even small deviations in the furnace temperature or fusion time have to be avoided as they may lead to significant changes in the concentration of elements. It should also be ensured that there are no delays when pouring the melt into the casting dish as this may impact the viscosity of the melt and thus increase the amount of residual material.

Especially for the preparation of samples with varying element composition it is critical to use effective cleaning mechanisms. Thus, different techniques were implemented to clean all components getting into contact with the sample material. For removal of residual powdery material we apply compressed air in conjunction with effective dust extraction. The casting dishes are passed over special rotating brushes to remove any remaining adhesions. The grinding vessel of the HP-MA can be purged with water compressed air, liquid or granulate depending on the sample type. The use of Mylar foil prevents sample spill-over and assists the efficient cleaning of the press tool.

In summary, the system makes full use of the advantages of pyrosulphate fusion. It not only enables reliable analytical results in routine laboratory operation but also leads to higher occupational safety and improved laboratory efficiency.

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