

Quantitative Analysis of FeMo Alloys by X-Ray Fluorescence Spectrometry

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Abstract

A quantitative analysis method of molybdenum in FeMo alloys by X-ray spectrometry using borate fusion technique was compared with that with pressed pellet. The complete pre-oxidation of FeMo alloys for the preparation of homogeneous fused discs was achieved by employing an automated fusion machine equipped with specially designed O₂-blowing nozzles, which used lithium tetraborate as flux with the addition of lithium nitrate (LiNO₃) as oxidizer. The calibration curves of Mo and Fe were used in the quantitative analysis of standard materials and unknown plant samples with satisfactory accuracy and precision, utilizing the corrections of the matrix effects and line overlap. It was confirmed that the newly proposed method of preparing fused glass discs of FeMo alloys can replace the conventional wet chemical analyses requiring the labor intensive and time consuming procedure.

Keywords

FeMo Alloys, X-Ray Fluorescence Spectrometry, Borate Fusion, Pre-Oxidation, Calibration Standard, Quantification

1. Introduction

As it has been required to develop and produce high performance steels for automotive, construction, engineering steel, offshore, packaging and so on, it is necessary to do in-depth research on new steel grades which improve physical properties such as high strength, high toughness, good corrosion resistance, and good formability [1] [2]. Because the physical properties of steel is directly determined by its microstructure, special treatments are applied to the steels for alloy composition adjustment, grain size control, steel cleanliness, deformation/texture control and control of segregation/intermetallic compound. In particular, the addition of ultrapure ferroalloys to liquid steel is of great essence for microalloying to provide specific mechanical properties to steel grade

[3]. One of the important alloying elements is molybdenum which is charged to liquid steel in the form of FeMo alloys. It is of great importance to accurately and reproducibly analyze Mo in FeMo alloys to control the final concentration of Mo in the ultimate steel grade to be aimed.

Most of the quantifications of Mo in FeMo alloys have been relied on wet chemical analysis such as KMnO_4 titration [4]. However, wet chemical analysis is labor-intensive and time-consuming work, and the use of toxic chemicals is very hazardous to humans. It has been demanded to convert the wet chemical analysis into the routine and automated instrumental analysis employing X-ray fluorescence (XRF) spectrometry by developing the borate fusion technique. In the case of fused disc preparation of ferroalloys, most of the ferroalloys mixed with oxidizer are stored in a muffle furnace of about 800°C overnight for preliminary oxidation of the samples, which also takes great care and time [5] [6]. Therefore, a rapid and automated fusion equipment is being attempted to be used for the integration of the complicated and stepwise procedure into one simple and routine preparation of fused discs for ferroalloys.

The current investigation aims to compare the XRF analysis by borate fusion method with that by pressed pellet from viewpoints of the sensitivity, accuracy and reproducibility for the analysis of Mo in FeMo alloys. Accordingly, it will be confirmed whether the conventional wet chemical analysis of molybdenum in FeMo alloys can efficiently be replaced with the XRF analysis using the homogeneous fused glass discs prepared in an automated fusion system equipped with specially designed O_2 -supplying apparatus.

2. Experimental

2.1. X-Ray Fluorescence Spectrometer

Bruker-AXS S4 Pioneer wavelength dispersive X-ray fluorescence spectrometer (WD-XRF) was employed in this research. The XRF was equipped with an end window Rh-target X-ray tube of the maximum output of 4 kW and eight diffracting crystals of various d-spacings. The measuring conditions and goniometer settings were programmed by the Bruker-AXS software “Spectra Plus” and summarized in **Table 1**. This application software was employed to calculate theoretical “variable alpha coefficients”. Alpha coefficients correct the absorption or enhancement of secondary radiation due to inter-element or matrix effects. The XRF was employed to measure the calibration standards in scan mode, and the optimal positions of highest signal intensities of peak and background were determined by overlapping the data files measured in scan mode. Subsequent XRF calibration and measurement were carried out in fixed mode.

Table 1. Summary of the spectrometer settings used in the present study.

Spectral lines	Mo		Fe	
	Pressed pellet	Borate fusion	Pressed pellet	Borate fusion
Sample preparation	Pressed pellet	Borate fusion	Pressed pellet	Borate fusion
Spectral line	Mo LA1-HR-Min (High resolution line)		Fe KA1-Maj (Majority line)	
Mode	Atmospheric He	Vacuum	Atmospheric He	Vacuum
Tube voltage (kV)	27	30	50	50
Tube current (mA)	112	77	10	8
Crystal (2d, Å)	PET (8.752)		LiF200 (4.026)	
Collimator aperture (degree)	0.23		0.23	
Detector	Flow		Scintillation	
Adjusted peak (2θ)	76.360	76.327	57.527	57.537
Wavelength (Å)	5.405		1.936	
Position of background (2θ)	77.612	74.542	58.470	58.346

2.2. Availability of Calibration Standards of FeMo Alloys for XRF Analysis

X-ray fluorescence spectrometry is a comparative measurement, which means that the quantification of elements is based on predetermined calibration curves constructed by using calibration standards. Therefore, the analysis of unknown FeMo alloys strongly depends on the availability of certified reference materials. In this study, nine calibration standards were used and their certified concentrations are listed in **Table 2**. The three Fe compositions marked by asterisks were analyzed in lab by ICP-AES (inductively coupled plasma-atomic emission spectroscopy) since the certified Fe concentrations were not available. This procedure is essential for XRF calibration because it is necessary to establish XRF calibration curves covering wide range of compositions and to simultaneously meet the requirement of variable alpha coefficient method for matrix corrections where the sum of all the compositions should lie in between 95 and 105 mass% for the calibration standards used [7].

2.3. XRD Patterns of a FeMo Alloy and a Calibration Standard

In most cases, X-ray fluorescence spectrometry analyzes the concentrations of cations or anions (e.g. Fe, Mo, etc.) and then converts them to those of compounds which are assumed to be most likely to exist in a sample. In order to identify the existing phases of Mo in FeMo alloys, X-ray diffraction analyses were performed for a FeMo alloy and a calibration (HC18605) as shown in **Figure 1**. The primary phase of Mo in both samples was estimated to be Fe_3Mo . This indicates that the effect of Mo existing in different forms on the matrix correction in XRF analysis will be minimized in case the pelletized FeMo alloys and calibration standards are directly measured by XRF. Therefore, it is straightforward to deal with Mo content in FeMo alloys and calibration standards where Mo only exists in the form of Fe_3Mo in the pressed pellet.

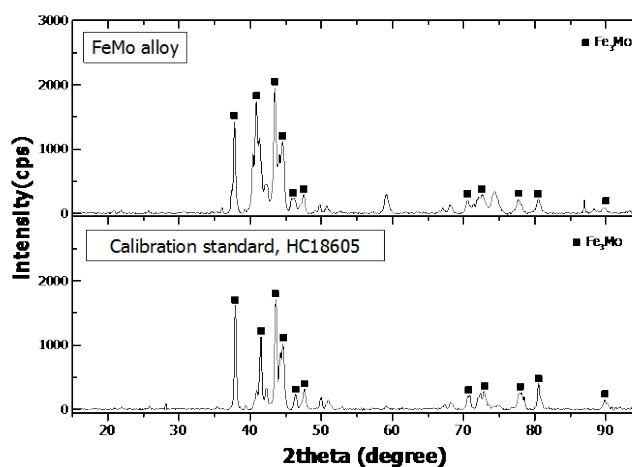


Figure 1. X-ray diffraction pattern of a FeMo alloy used in secondary steelmaking process and one of the standard reference materials employed in the current study.

Table 2. Compositions of calibration standards of FeMo alloys available in markets.

Calibration standards	Composition (mass %)									
	Mo	Fe	C	Si	S	P	Mn	Ni	Cr	Cu
HC18605	55.78	42.53	0.015	0.055	0.079	0.154	-	-	-	0.63
SL20-13	60.03	38.42	0.029	0.28	0.081	0.039	0.012	0.017	0.05	0.4
SL20-20	62.20	36.71	0.028	0.21	0.079	0.034	0.013	0.019	0.057	0.376
HC26610	66.52	31.59	0.049	1.20	0.064	0.034	-	-	-	0.52
SL20-12	69.99	27.82	0.011	0.79	0.084	0.028	0.042	-	-	0.39
E578-1	72.23	26.46	0.016	0.208	0.065	0.024	-	-	-	0.136
SL20-08	72.82	25.51	0.018	0.71	0.059	0.017	0.088	0.02	0.039	0.378
SL20-06	73.83	24.03	0.031	0.252	-	0.086	0.07	0.905	0.018	0.134
SL20-10	78.09	20.66	0.026	0.161	0.092	0.017	0.010	0.112	0.035	0.464

3. Results and Discussion

3.1. Preparation Procedure of Pressed Pellet of FeMo Alloys

Powdered samples constitute one of the most frequently used specimen forms in x-ray spectrometry. Powders are more often analyzed as a pressed pellet. To achieve a uniform small particle size, the pulverization is carried out. It is not unreasonable to expect a relationship between fluorescent x-ray intensity and particle size since x-rays can only penetrate and emerge from a finite depth beneath the surface. Although there have been several theoretical effects of particle size and size distribution upon x-ray spectrochemical analysis results [8] [9], the qualitative effects of particle size on the spectral line intensity can be alleviated in most cases by reduction of the entire sample to sub-10 μm particles. The detailed procedure is as follows:

- The nine calibration standards have been pulverized for about 1 h by employing a planetary ball mill technique so that the particle size was decreased to approximately less than 10 μm .
- For the XRF measurement of samples in the form of pressed pellets, boric acid powder was first lightly packed to a 40 mm aluminum cup inside a 42 mm ID cylindrical die.
- An accurately weighed portion of each sample was added in sufficient amount to cover the top of the boric acid powder.
- A plunger was inserted into the die and hydraulic pressure was applied in a briquetting press (Herzog, maximum pressure 40 ton).
- Only one face of sample material in the resulting sample disc encased in an aluminum dish was exposed to X-ray radiation for analysis.
- Briquettes formed in this manner remained intact after repeated analyses, provided they were stored in a desiccator.

3.2. Calibration for Pelletized FeMo Alloys and Evaluation of Their Validity

The calibration curves of Mo and Fe in the form of pressed pellet are presented in **Figure 2** based on the calibration conditions summarized in **Table 3**. Each calibration curve was obtained by applying matrix corrections with the help of variable alpha coefficient method and line overlap compensation. The linearity of Mo and Fe calibration curves were improved by removing three and two points out of the entire calibration standards, respectively. From the viewpoints of standard deviation resulted from the calibration curves in **Table 3** and squared correlation coefficient values in **Figure 2**, the case of Fe shows better results in comparison with that of Mo. It is believed that this is ascribed to the higher sensitivity of Fe-KA1-Major line compared with Mo-LA1-HR (high resolution)-Major line, which will be discussed later. From the relative linear correlations between corrected X-ray intensity and concentrations of Mo and Fe for the investigated compositional range of each component, it was believed that XRF calibration using pressed pellet can approximately be applied for the chemical analysis of FeMo alloys.

Table 3. Calibration data for Mo and Fe in the original sample.

Spectral line	Mo LA1-HR-Maj		Fe-KA1-Maj	
	Pressed pellet	Borate fusion	Pressed pellet	Borate fusion
Sample preparation	Pressed pellet	Borate fusion	Pressed pellet	Borate fusion
Absorption correction	Variable alpha		Variable alpha	
Intensity model	Net intensity		Net intensity	
Minimization target (mass %)	Absolute error, 6 standards from 55.78 to 73.83	Absolute error, 9 standards from 55.78 to 77.64	Absolute error, 7 standards from 20.66 to 42.53	Absolute error, 9 standards from 20.66 to 42.53
Standard deviation (mass %)	1.53	0.45	0.557	0.400
Sensitivity (KCps/%)	1.668	0.212	10.16	0.367
Corrected intensity offset	-87.8 KCps	-	-18.79 KCps	0.017 KCps
Line overlap correction	None	S KA1	Mn KB1	-

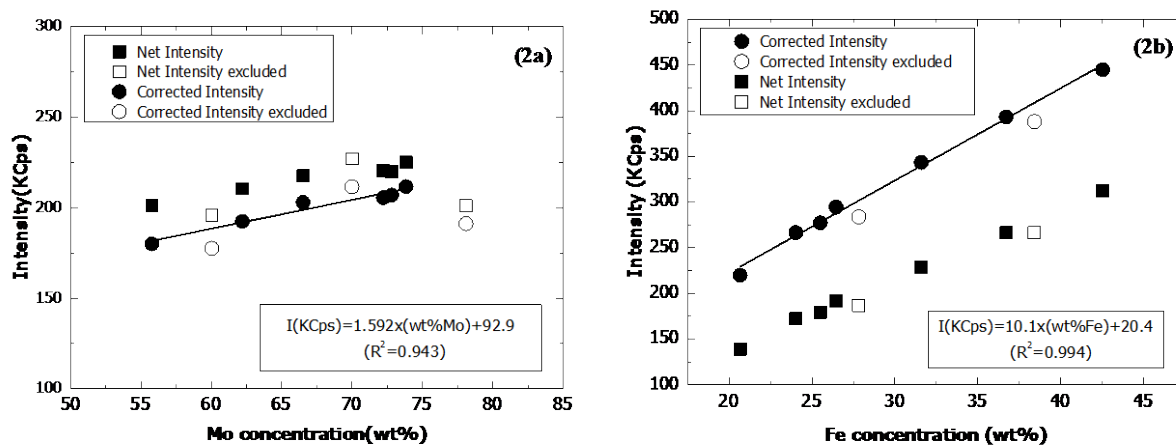


Figure 2. XRF Calibration curves of Mo (a) and Fe (b) using pressed pellet with matrix effects and line overlap corrections.

In order to evaluate the validity of the XRF calibration curves, three repeated XRF measurements were made on one of the calibration standards used. As shown in **Table 4**, XRF analyses of the calibration standard (SL20-20) are quite precise since all the precision RSD ($RSD (\%) = (\text{standard deviation}) / \text{average} \times 100$) values for Mo and Fe values from each constituent show less than about 0.5%. Therefore, the XRF calibration curves using the calibration standards can be utilized for the quantitative chemical analysis of Mo and Fe in FeMo alloys with acceptable precision for the quality control of FeMo production process.

3.3. Preparation Procedure of Glass Discs by Borate Fusion Technique

The borate fusion technique has been employed to eliminate particle size and mineralogical effects. In the case of ferro alloys, due to the interaction between the sample and Pt crucible during fusion, the pre-oxidation of the sample in a muffle furnace for overnight requires a time-consuming and labor-intensive work as previously mentioned. Therefore, the specially designed O_2 -supplying nozzles were additionally installed over the platinum crucibles in order to ensure the complete oxidation of the FeMo samples during the preparation of the fused discs. The detailed preparation procedure of the newly proposed fusion is as follows:

About 10 g of lithium tetraborate ($Li_2B_4O_7$) were first weighed in a platinum crucible (5% Au/Pt) and then a spatula was used to form a solid wall of the flux.

- 0.11 g of non-wetting agent (LiBr) was put onto the flux and then 1.5 g of oxidizer ($LiNO_3$) was added into the platinum crucible.

- 0.3 g of FeMo sample was put in the crucible (dilution factor = 1/33) and mixed with the oxidizer. The overall composition and cooling conditions must be such that the end product after cooling is a homogenous glass disc.

- As shown in **Figure 3**, the platinum crucible containing the flux, non-wetting agent, oxidizer and sample started to be heated up to $615^\circ C$ for 10 min and then the temperature was slowly raised up to $850^\circ C$ in O_2 -blowing atmosphere (1 l/min) for 45 min for ensuring the complete pre-oxidation of the sample.

- Then the crucible was quickly heated up to $1000^\circ C$ and held at the temperature for 3 min, then being followed by the pouring of the melt into a platinum mold.

- Right after the fused melt started to be naturally cooled down, the rapid cooling was employed by fan cooling from the bottom of the mold for easy release of the quenched disc from the platinum mold.

Infrared spectroscopy has been extensively employed over the years to investigate the glass structures. In particular, borate glasses have been the subject of numerous infrared studies, due to their structural peculiarities [10] [11]. Although sufficient homogenization in liquid borate melt is carried out during fusion, some crystallization might be resulted in the glass disc during cooling. Therefore, the current study employed FT-IR spectroscopy to confirm whether the fused glass is really homogeneous across the disc surface to be exposed to the XRF radiation as shown in **Figure 4**. That is, the measured data for five positions on the disc by FT-IR spectroscopy indicate that some functional groups (O-B-O ring bending, symmetric and asymmetric stretching) were clearly identified over the specific spectral range, which are typical spectral peaks for borate glasses. As is clearly noticed,

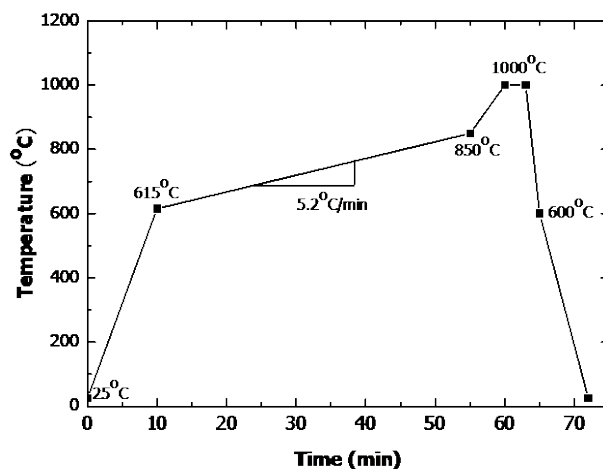


Figure 3. Heating and cooling profiles of the automated fusion system for preparing the fused discs of FeMo alloys using Kanax K₂ equipped with O₂-supplying nozzles over fusion stations.

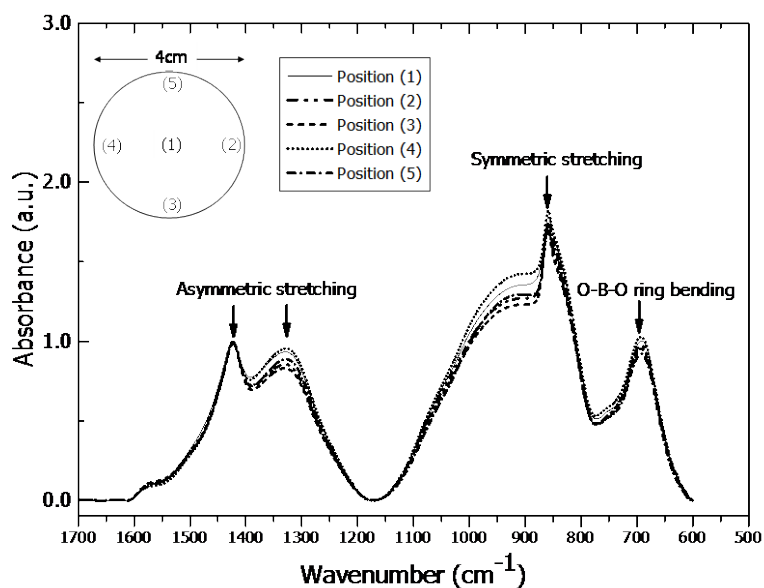


Figure 4. Homogeneity testing of the borate fusion disc of a calibration standard (SL20-20) employing FT-IR spectroscopy.

Table 4. Precision and accuracy tests for a calibration standard (SL20-20) by three XRF measurements using pressed pellet and borate fusion (units: mass%).

Elements	Mo (Certified conc. = 62.20 mass %)		Fe (Certified conc. = 36.71 mass %)	
	Pressed pellet	Borate fusion	Pressed pellet	Borate fusion
Test_01	62.87	62.07	36.73	36.41
Test_02	62.85	62.02	36.78	36.50
Test_03	63.20	62.02	36.76	36.48
Average	62.97	62.04	36.76	36.46
Standard deviation	0.19	0.02	0.03	0.04
Precision RSD (%)	0.31	0.04	0.07	0.11

there is no remarkable difference among the IR spectra for the five positions. This strongly indicates that the fused disc is homogeneous enough to be used for XRF calibration and analyses and that the newly proposed fusion method of FeMo alloys can be applied for the reliable preparation of borate glass for XRF analysis of FeMo alloys.

3.4. Calibration for Fused Glass Discs of FeMo Alloys and Evaluation of Their Validity

The nine calibration standards were fused into glass discs by lithium borate fusion technique, and the calibration curves of Mo and Fe were constructed as shown in **Figure 5**. Each calibration curve was obtained by applying matrix corrections with the help of variable alpha coefficient method and line overlap corrections. Both of them indicate good linear correlations between corrected X-ray intensity and concentrations of Mo and Fe for the investigated compositional range of each component. Therefore, it is believed that the nine standard materials in the form of fused glass disc can appropriately be applied to XRF calibration for the chemical analysis of FeMo alloys.

As is similar to the case of pressed pellets, the validity of the XRF calibration curves was evaluated by making three repeated XRF measurements on one of the standards (SL20-20) used for XRF calibration. As shown in **Table 4**, XRF analyses of the FeMo alloy components are quite precise since both the relative standard deviation (RSD) values for Mo and Fe show less than about 0.5%. In **Table 4**, the analysis results by XRF are comparable to the certified concentrations of Mo and Fe, and can be acceptable considering that small portion of the Mo samples might vaporize during borate fusion process. Therefore, the XRF calibration curves using all the nine standards can be utilized for the quantitative chemical analysis of Mo and Fe in FeMo alloys with acceptable precision and accuracy for the sake of quality control of Mo microalloying in secondary steelmaking processes.

3.5. Comparison of Sensitivity, Accuracy and Precision between Pressed Pellet and Fused Disc

In case the borate fusion technique is employed for the sample preparation of X-ray spectrometry, the spectral signal of low concentration of fluorine in stainless steelmaking slags might not be detected due to its low sensitivity [12]. Sensitivity is defined as the fractional change in instrument response per unit change in concentration of the measured element [7]. Accordingly, the slopes of the calibration lines in **Figure 2** and **Figure 5** correspond to the sensitivities of the selected spectral lines of respective element in FeMo alloys.

In order to figure out how the sample preparation methods affect the sensitivity of each spectral line, the comparison was made between the calibration lines constructed by borate fusion technique and those by pressed pellet. As obviously noticed in **Figure 6**, the sensitivities of spectral lines of Mo and Fe decreased by about 6 and 27 times, respectively, although the dilution ratio of sample to borate fusion flux is 1 to 33. That is, the sensitivity of Mo LA1-HR line decreased less compared with the dilution ratio and the linearity of the Mo calibra-

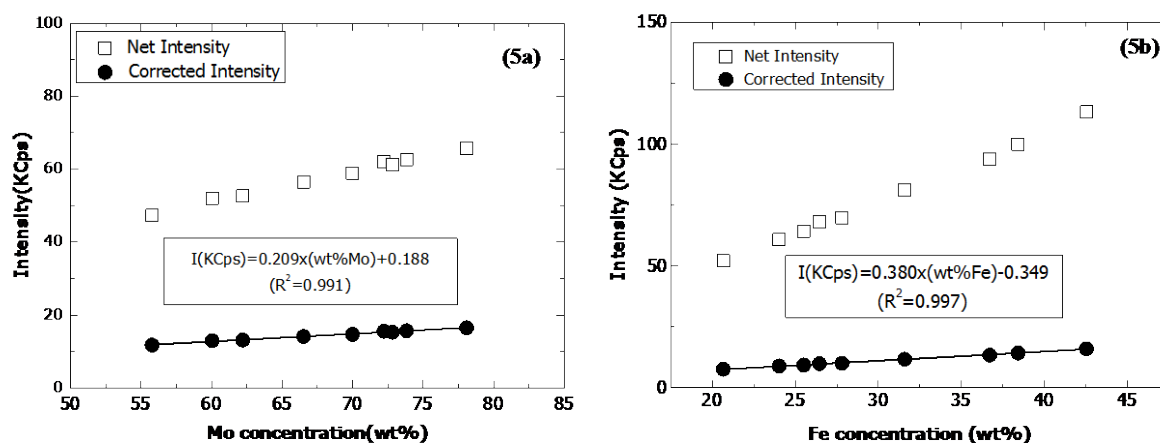


Figure 5. XRF Calibration curves of Mo (a) and Fe (b) using borate fusion technique with matrix effects and line overlap corrections.

tion line using borate fusion technique was improved as clearly compared in **Figure 2** and **Figure 5**. This indicates that the measured intensity of Mo in the form of borate fused discs was nicely corrected by applying variable alpha coefficients and line overlap calculation against Mo concentration in the calibration standards.

Once the calibration curves of the specific elements in a material are successfully established using the pressed pellet and borate fusion technique, the subsequent step is to actually analyze unknown samples by XRF spectrometry and to compare them with the results certified by wet chemical analysis. As shown in **Table 5**, two unknown FeMo alloys to be used in secondary steelmaking plants were analyzed by XRF using both the preparation methods and compared with the results obtained by wet chemical analysis of Mo [4]. In both the samples, the analyzed Mo content by XRF using the borate fusion method is much closer to that determined by wet chemical analysis compared with that using pressed pellet. However, from a viewpoint of precision of the data, there is no great difference in the standard deviation between pressed pellet and borate fusion method. Therefore, in the actual operational situation of sophisticated charging of FeMo alloys in secondary steelmaking plants, the suggested preparation using borate fusion for the Mo analysis by XRF could be more reliable in case the rapid and routine analysis of Mo should be carried out. That is, the calibration curves of Mo and Fe can be utilized for the quantitative chemical analyses of Mo and Fe in FeMo alloys depending on the precision and accuracy to be aimed for the quality control of secondary steelmaking process.

4. Conclusion

X-ray fluorescence spectrometry of FeMo alloys employing an automated fusion system equipped with O₂-supplying nozzles was compared with that using pressed pellet. From the findings, the following conclusions were obtained. From the viewpoints of standard deviations and squared correlation coefficient values resulted from the calibration curves of Mo and Fe using pressed pellet, the case of Fe shows better results in comparison with that of Mo, which is ascribed to the higher sensitivity of Fe-KA1 line compared with Mo-LA1-HR (high resolution) line. The complete oxidation of FeMo alloys by adding oxidant and by employing O₂-supplying apparatus made contribution to the preparation of the fused discs, whose homogeneity was confirmed by FT-IR spectroscopy. The measured intensity of Mo in the form of borate fused discs was nicely corrected by applying variable alpha coefficients and line overlap calculation against Mo concentration in the calibration standards.

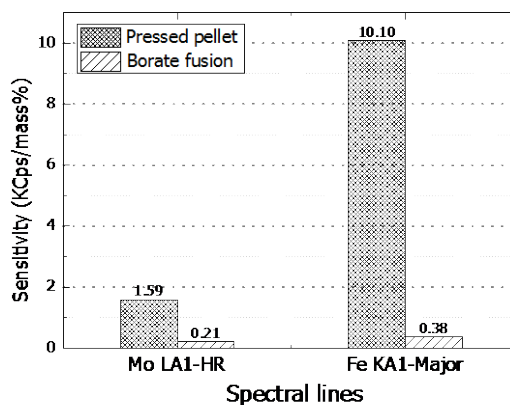


Figure 6. Comparison of the sensitivities of each spectral line (Mo and Fe) affected by sample preparation methods (Pressed pellet vs Borate fusion).

Table 5. Comparison of the analysis results of plant unknown FeMo alloys by wet chemical analysis and XRF measurement.

Unknown samples	Mo conc. by wet chemical analysis (mass %) [4]	Mo content by XRF (mass %)	
		Pressed pellet	Borate fusion
FeMo1	60.99	60.42 ($\pm 0.05^*$)	60.90 ($\pm 0.13^*$)
FeMo2	64.33	62.24 ($\pm 0.14^*$)	63.99 ($\pm 0.11^*$)

*represents the standard deviations produced by three repeated measurements using the respective preparation methods.

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