

Determination of Molybdenum in Iron and Steel with Vacuum Spectrometer

著者	GOTO Hidehiro, SAITO Akira
journal or publication title	Science reports of the Research Institutes, Tohoku University. Ser. A, Physics, chemistry and metallurgy
volume	20
page range	14-21
year	1968
URL	http://hdl.handle.net/10097/27414

Determination of Molybdenum in Iron and Steel with Vacuum Spectrometer*

Hidehiro GOTÔ and Akira SAITÔ

The Research Institute for Iron, Steel and Other Metals

(Received April 30, 1968)

Synopsis

In the direct-reading spectrometric determination of molybdenum, the overlapping spectral lines of nickel and manganese often interfere with analytical results. In this paper, analytical lines of molybdenum, Mo II 2038.46 Å and Mo II 2020.32 Å, are newly proposed, making use of iron line Fe II 1761.38 Å as an internal standard. With these spectral lines, interfering elements, excitation conditions, and reproducibility of the results were investigated.

The best results were obtained under the excitation of the critically damped discharge of a low voltage condenser spark. The overlapping line of manganese slightly interfered with Mo II 2038.46 Å. With Mo II 2020.32 Å, which had no interfering element, 0.20% and 1.09% of molybdenum in low alloy steels were determined with the variation coefficients of 2.2% and 1.6%, respectively.

I. Introduction

The addition of molybdenum to a steel can improve its physical properties, and therefore, 10^{-2} ~several per cent of molybdenum is usually added to many kinds of steel. It is important for the steel making process to know the molybdenum content accurately and rapidly. In this sense, the analysis of molybdenum in iron and steel has been carried out by the direct-reading spectrometry. As the analytical spectral lines, Mo II 2775.400 Å and Mo II 2816.154 Å have mainly been used in the routine analysis; however, the overlapping spectral lines of nickel and manganese⁽²⁾ interfere with the former and those of aluminium and manganese⁽²⁾ interfere with the latter. In some steels, contents of manganese and nickel are so high that a suitable correction should be done for the accurate analysis of molybdenum. Otherwise, it is necessary to find out a new analytical line which has no interfering line. From this point of view, the present investigations were carried out to find out a proper analytical line in the wavelength near 2000 Å and to apply it to the spectrometric determination of molybdenum in iron and steel.

* The 1361st report of the Research Institute for Iron, Steel and Other Metals. Reported in the Japan Analyst, **17** (1968), 194, in Japanese.

(1) S. Maekawa and T. Suzuki, Bunko Kenkyu, **11** (1962), 61.

(2) Japan Industrial Standards, G 1252 (1959).

II. Instruments and samples

1. Instruments

Shimadzu's high-precision electric discharge source unit and Shimadzu's high-vacuum ultraviolet spectrometer (EGV-200)⁽³⁾ were used. The spectrometer is Eagle mounting type which has three photomultiplier tubes and an entrance lens of calcium fluoride, and can be evacuated to 2.5×10^{-5} mmHg. It has the Bausch and Lomb's concave grating of 2.0 m of curvature radius, 1200 lines/mm of groove number, 40×80 mm of grooving area, 1700 Å of blaze wavelength, and degree of dispersion of 4 Å/mm. In the present investigation, two photomultiplier tubes were used, one having an exit slit of 40μ for the analytical spectral line and the other having an exit slit of 60μ for the internal spectral line.

2. Samples

The samples used were of disc form, 25 mm in diameter and 10 mm in thickness, and finished with belt grinder of 80 mesh emery.

III. Experimental and discussion

1. Spectral lines of molybdenum

The spectral lines of molybdenum was examined over the range of 2000Å to 1780Å, and eleven intense lines were observed in the range of 2200Å to 2000Å as shown in Table 1, while no intense line was found below 2000 Å. In Table 1, the wavelength and the intensity were quoted from a reference⁽⁴⁾, and the excitation potential was calculated from the energy levels tabulated in the reference.

Table 1. Intense spectral lines of molybdenum in the wavelength range of 2200Å to 2000Å

Wavelength (Å)	Intensity	Excitation potential (eV)	Interfering element
MoII 2197.48	100	8.94	Fe, Ni
MoII 2189.40	50	8.54	W, Cu
MoII 2184.36	100	7.62	Fe, Ni
MoII 2125.92	75	8.68	Ni, Cu, W
MoII 2108.04	50	8.76	Fe
MoII 2100.83	50	7.81	{ Fe, W
MoII 2100.70	30	7.80	
MoII 2093.11	50	8.74	Fe, Ni, Co
MoII 2045.98	75	—	Fe, V
MoII 2038.46	75	6.08	(Co, Mn)
MoII 2020.32	100	6.13	—
MoII 2015.12	50	6.15	Fe, Cu, V

(3) H. Gotô, S. Ikeda, K. Hirokawa, H. Seno and A. Kaya, Sci. Rep. RITU, **A 17** (1965), 96.

(4) C.C. Kiess, J. Res. NBS, **60** (1958), 375.

Interfering elements were searched for in the wavelength tables^(5,6). The spectral lines of 2038.46Å and 2020.32Å have lower interfering elements than the other lines as shown in Table 1. Therefore, these spectral lines, which belong to the same multiplet and come from S-P transition were examined. The spectral profiles near Mo II 2038.46Å and Mo II 2020.32Å of low alloy steels are shown in Figs. 1 and 2, respectively.

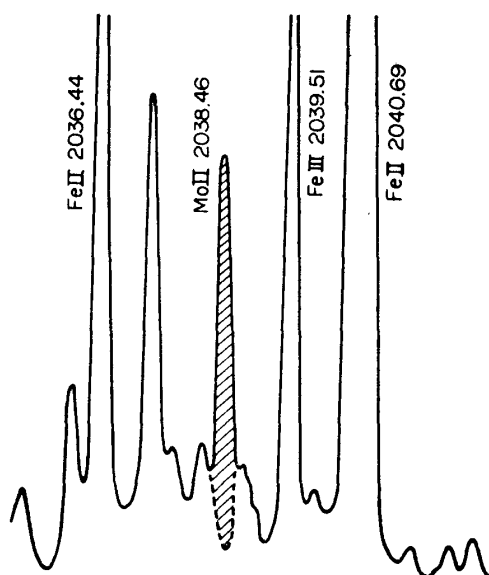


Fig. 1. Profile of Mo II 2038.46Å spectral line in iron and steel samples (1.50%Mo)

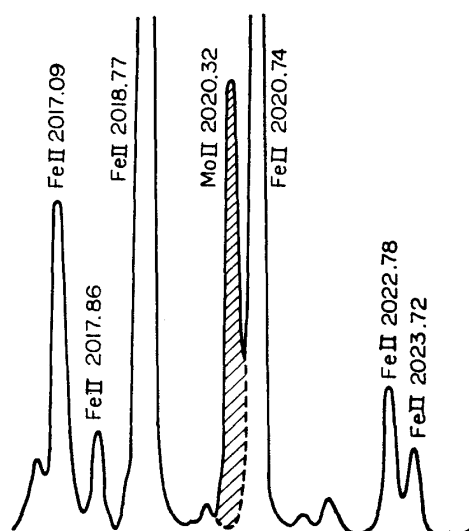


Fig. 2. Profile of Mo II 2020.32Å spectral line in iron and steel samples (1.09%Mo)

2. Investigation with Mo II 2038.46Å

Considering usable wavelength range and excitation potential, Fe II 1761.38 Å (excitation potential: 9.03 eV) was selected out as an internal spectral line. As the excitation conditions, high voltage spark discharge (H.V. S.), and three kinds of low voltage condenser spark discharge (L.V.S.) were used. The excitation conditions and the circuit parameters of discharge are listed in Table 2. The standard

Table 2. Excitation conditions

	H.V.S.	L.V.S.		
		(1)	(2)	(3)
Capacitance (μF)	0.007	10	10	40
Reactance (μH)	860	50	50	50
Resistance (Ω)	residual	3	5	25
Voltage (V)	20k	900	900	900
Counter electrode	6mm ϕ Ag (120° cone)			
Spark gap	2mm			
Atmosphere	10%Ar/min			

(5) M.I.T. Wavelength Tables.

(6) N.B.S. Ultraviolet multiplet table.

Table 3. Chemical composition of low alloy steel samples

No.	Mo (%)	C (%)	P (%)	S (%)	Si (%)	Mn (%)	Cu (%)	Cr (%)	Ni (%)	W (%)
80	1.50	0.02	0.005	0.016	0.01	1.07	0.01	0.53	0.08	0.10
81	1.09	0.07	0.009	0.012	0.24	0.71	0.05	0.56	0.44	0.14
82	0.57	0.16	0.018	0.009	0.03	1.24	0.06	0.34	1.51	0.90
83	0.31	0.37	0.039	0.017	0.31	0.68	0.22	2.36	0.14	0.20
84	0.15	1.24	0.054	0.041	0.49	0.45	0.20	1.44	0.43	0.18
85	0.06	0.73	0.092	0.073	1.29	0.37	0.78	0.19	0.23	1.57

samples of low alloy steel shown in Table 3 were used for the preparation of calibration curves. The calibration curves under various conditions of excitation are shown in Fig. 3-(a), (b), (c), (d).

In the high voltage spark discharge (a), the calibration curve showed considerably large deviations of each value and high background. In the oscillating discharge of low voltage spark (b), no difference from (a) was noticed except for the lower background. In the critically damped discharge (c), the calibration curve showed a more steep inclination and a better rectilinearity. In the over-damped discharge (d), the calibration curve had the most steep inclination and the lowest background, but, it curved in the high content of molybdenum.

In the result, it was clarified that the critically damped discharge of low voltage with a circuit parameter of C: $10\mu\text{F}$, L: $50\mu\text{H}$, R: 50Ω was the most suitable condition. Moreover, the coexistence of almost 1 per cent of manganese and nickel did not interfere with the determination of 0.3 to 1.5 per cent of molybdenum.

In the next experiment, the determination of lower content of molybdenum was tried with the low alloy steels 116~168 of N.B.S. for spectrographic analysis. The resultant calibration curve is shown by the mark \bullet in Fig. 4. In this figure, considerably large deviations of each point are noticed. Especially, three samples (1162~1164) of these show large deviations. The analysis⁽⁷⁾ of the data showed that the deviations were due to the presence of manganese. Quantitatively, 1 per cent of manganese was equivalent to 0.022 per cent of molybdenum. The interfering spectral line of manganese may be Mn II 2038.87Å. By correcting the interference of manganese, a rectilinear calibration curve was obtained as plotted with the mark \circ in Fig. 4. This result also showed that the nickel contents below 2 per cent did not interfere with the analysis of molybdenum.

3. Investigation with Mo II 2020.32Å

As shown in Table 1, Mo II 2020.32 Å should have more useful applicability as an analytical line, because of no interfering line and stronger intensity. The line Mo II 2020.32Å belongs to the same multiplet and, accordingly, its excitation potential is so close to that of Mo II 2038.46Å that a further examination of excitation condition was not undertaken. Therefore, the experiments were

(7) H. Gotô and A. Saitô, Sci. Rep. RITU, A 19 (1967), 226.

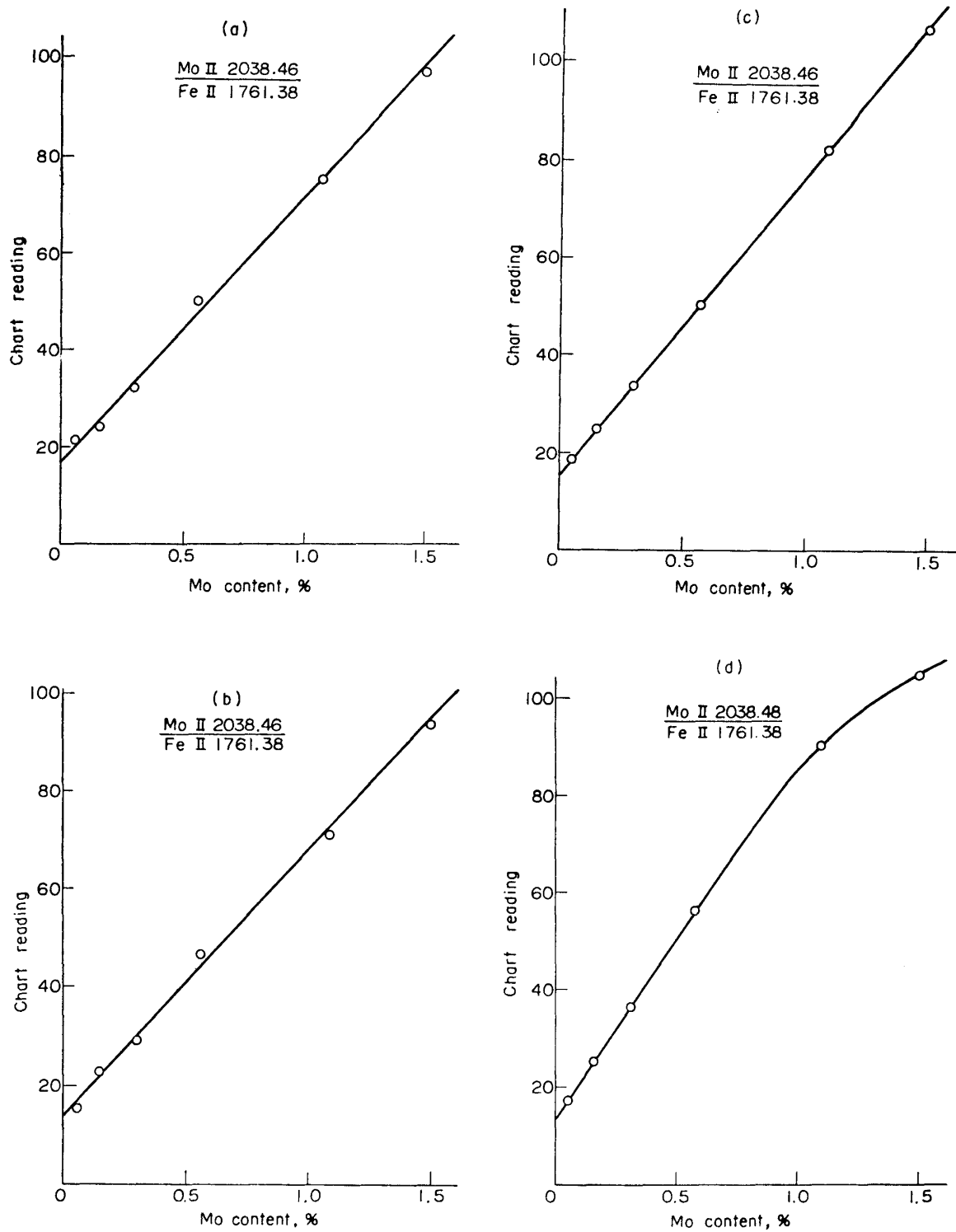


Fig. 3. Calibration curves for molybdenum in various excitation conditions (a) High voltage spark (H.V.S.), (b) Low voltage oscillating discharge (L.V.S.I), (c) Low voltage critically damped discharge (L.V.S.2), (d) Low voltage over damped discharge (L.V.S.3)

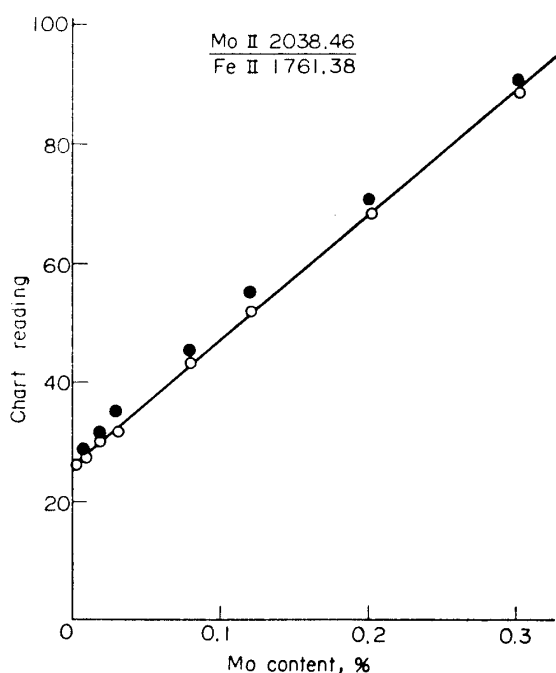


Fig. 4. Calibration curve for molybdenum before and after the correction for manganese • Before correction, o After correction, Excitation condition : L, V, S, 2

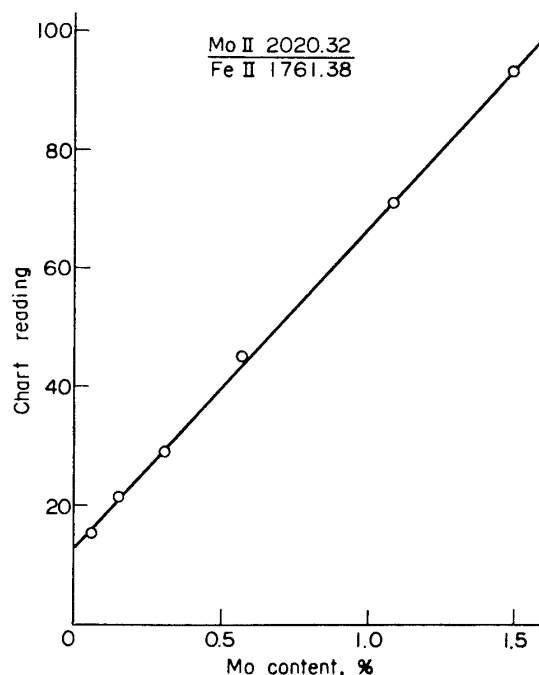


Fig. 5. Calibration curve for molybdenum in the concentration range of below 1.5% Mo Excitation condition : L, V, S, 2

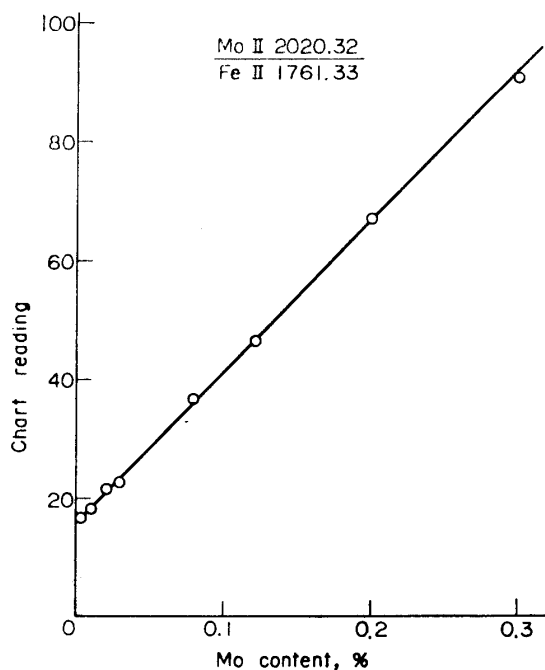


Fig. 6. Calibration curve for molybdenum in the concentration of below 0.3% Mo Excitation condition : L, V, S, 2

carried out under the same excitation condition as in the case of Mo II 2034.46Å. Namely, the excitation condition was the critically damped discharge of the low voltage spark (C: 10μF, L: 50μH, R: 5Ω) which was the most suitable for

Mo II 2038.46 Å. The calibration curve for the low alloy steel shown in Table 3 is shown in Fig. 5. In this case, the rectilinearity was very well, similar to the case of the Mo II 2038.46 Å. Moreover, under the same condition a calibration curve was prepared with the N.B.S. standard samples and is shown in Fig. 6. The calibration curve obtained had a good linearity having no interference of manganese.

To test the precision and the accuracy of the analysis, twelve measurements were finally carried out with two standard samples. These results are shown in Table 4. For the standard sample of 1.09% Mo, the mean value of 1.09% and the coefficient of variation of 1.6%, and for the standard value of 0.20% Mo, the mean value of 0.20%, and the coefficient of variation of 2.2% were obtained. These data show that the Mo II 2020.38 Å has a good precision and accuracy. The comparison of this spectral line with the Mo II 2038.46 Å showed the low background, 1.25 times in intensity, and no interfering elements. Therefore, the spectral line Mo II 2020.32 Å is useful as the analytical line of molybdenum.

Table 4. Reproducibility of the determination of molybdenum with the line pair of Mo II 2020.32/Fe II 1761.38

Sample	Low alloy steel No. 81	NBS 1168
Mo content (%)	1.09	0.20
	1.08	0.20
	1.09	0.20
	1.10	0.20
	1.06	0.21
	1.10	0.20
Observed value (%)	1.12	0.20
	1.10	0.20
	1.06	0.20
	1.12	0.20
	1.08	0.19
	1.09	0.20
Mean value \bar{x} (%)	1.08	0.20
Std. dev. σ (%)	0.017	0.0043
$\sigma/\bar{x} \times 100$ (%)	1.6	2.2

IV. Conclusion

The investigations on the emission spectrometric analysis of molybdenum in iron and steel were carried out for the spectral lines of molybdenum in wavelength below 2200 Å, and the following results were obtained.

(1) Eleven intense spectral lines of molybdenum were noticed in the range of 2200 to 2000 Å. Of these lines, Mo II 2038.46 Å and Mo II 2020.32 Å were examined in the sense of the analytical property. The latter was more useful than the former which had interference line of Mn III 2038.87 Å and a little lower intensity.

(2) The condenser spark discharge of low voltage with the circuit parameter of C: $10\ \mu\text{F}$, L: $50\ \mu\text{H}$, R: $5\ \Omega$ was the most suitable.

(3) Using the spectral line of Mo II $2020.32\ \text{\AA}$ the molybdenum content of 0.20% and 1.09% could be analyzed in the precision of 2.2% and 1.6% of variation coefficient, respectively. Therefore, this is usable in the spectrometric analysis of molybdenum in iron and steel.