

Multi-Element Trace Analysis in Molybdenum Matrix by Inductively Coupled Plasma Atomic Emission Spectrometry

Zun Ung Bae, Sung Ho Lee[†], and Sang Hak Lee

Department of Chemistry, Kyungpook National University, Taegu 702-701, Korea

[†]Central Research Institute, Korea Tungsten Co., Dalsung, Kyungpook 711-860, Korea

Received March 28, 1995

A method for the direct determination of trace amounts in molybdenum matrix by inductively coupled plasma atomic emission spectroscopy is described with emphasis on line selection and spectral interferences. Metal samples were decomposed by microwave-assisted sample digestion method. The spectral interference coefficients were calculated for the 270 spectral lines of 67 elements and these values were used for line selection and to calibrate concentrations of the analytes. The limits of detection of the elements for this method were determined and compared with those obtained by flame atomic absorption spectrometry and direct current carbon arc emission spectroscopy. Analytical reliability of the proposed method was estimated by analyzing a spiked solution and the results indicated that the accuracy of multi-element analysis is satisfactory.

Introduction

Molybdenum is of great importance in various branches of industry, particularly in the production of special steels, super conducting materials and high-temperature alloys.¹ It may be used as an inner wall in nuclear fusion reactor and as gate materials in metal oxide semiconductor-very large scale integration technology. Molybdenum trioxide has been used as a catalyzer and an intermediate for the production of metallic Mo. A detailed knowledge of the levels of the trace elements in raw materials and the finished products is essential since they may have either a deleterious or beneficial effect upon the mechanical and physical properties of the end metallurgical product.²⁻⁴ Therefore, there is currently a strong interest in the determination of trace elements in molybdenum and its related compounds⁵⁻⁸ such as molybdenum trioxide and molybdenum silicide.

Trace element analysis of these materials is not an easy task due to the difficulty of dissolution and the instability of the sample solutions. The analysis of these materials by atomic emission spectrometry is difficult due to the complex nature of the emission spectra giving rise to coincidences with the analyte wavelengths. A matrix separation method using a complexing agent such as cuperron can be considered in order to avoid spectral-line interferences. However, coprecipitation of other trace elements of interest also might be occurred. Cation-exchange chromatographic method⁹⁻¹⁰ might be used to separate the analytes from Mo followed by various detection techniques such as spectrophotometry and atomic absorption spectrometry. However, ion-exchange procedure is tedious and might not give sufficient precision and accuracy of quantitative results. Activation analysis does exhibit many advantages in terms of high accuracy results. However, this method is difficult to apply to industrial control of materials since analysis can take weeks if long-lived isotopes have to be determined.

Inductively coupled plasma atomic emission spectroscopy (ICP-AES) is recently the most reliable tool in the determination of trace elements. Since a current limitation of using ICP-AES is the spectral interferences observed with elements

that emit line-rich spectra, line selection is a major problem in this method. A few papers¹¹⁻¹³ have been published on this topic. Ullmann and Ringer¹¹ have used a high-resolution monochromator for the direct determination of 27 elements in pure tungsten. A 3600 lines mm⁻¹ interferometric grating was set up in the 1 m monochromator and used in the first order with entrance and exit slit widths of 10 and 25 μm , respectively. Line selection and limits of detection were given. Brenner and coworkers¹² have used a polychromator and a monochromator for the determination of elements in pure tungsten and related materials. Sample preparation, line selection, precision and limits of detection were reported. Some examples of spectral scans were also given to illustrate the difficulty of obtaining lines free from spectral interferences. Recently Carre *et al.*¹³ used an ICP system equipped with a high resolution 1 m monochromator set up with a 2400 lines mm⁻¹ interferometric grating. This grating was utilized in the second order for wavelengths shorter than 300 nm. They searched line selection and spectral interferences for 19 elements in tungsten matrix and classified into line coincidence, partial overlap or shoulder, wing interference and full separation. However, an analytical evaluation of the selected analytical lines in terms of the interferences from spectral lines of various trace elements in molybdenum matrix was not investigated.

In this study, we searched interfering spectral lines for nearly all of the elements in molybdenum matrix that can be determined by ICP-AES. For the analytical lines of trace elements of interest we calculated spectral interference correction coefficients (K_{ij}) to estimate the amount of spectral interferences on the individual lines. In order to carry out recovery studies, the synthetic solutions containing certified amounts of the analytes of interest were made and the corrected concentrations of the elements were obtained using the K_{ij} values. The results were compared with those obtained by other analytical methods such as flame atomic absorption spectrometry (FAAS) and direct current carbon arc atomic emission spectrometry (d.c. arc AES). The limits of detection for the analytes were evaluated for the procedure suggested in this paper and the technique was applied to

the analysis of real samples.

Experimental

ICP-AES. A Jobin-Yvon JY 38 Plus ICP system was employed. It consists of 40.68 MHz radio frequency generator, a demountable torch with argon sheath system and a high resolution 1 m monochromator equipped with a 2400 lines mm^{-1} holographic grating for the line selection and determination of trace elements. This grating was utilized in the second order for wavelengths shorter than 300 nm. Both of the entrance and exit slit widths were 20 μm . Spectral scans, using a 2 pm step, were performed over a range of 60 pm with an observation height 15 mm above the load coil. Argon gas was used to purge the optical path and the monochromator for wavelengths in the range 180-195 nm. Because solutions containing hydrofluoric acid were employed in the present study a hydrofluoric acid resistant sample introduction system was used. This system consists of a platinum-iridium concentric nebulizer (Jobin-Yvon, Cat. No. 20925080), a PTFE nozzle, a scott-type coaxial plastic spray chamber (Jobin-Yvon, Cat. No. 11285268), a plastic sheathing tube and a sapphire sample introduction tube. A force fed Miniplus II peristaltic pump (Jobin-Yvon, Cat. No. 21357000) was used to deliver sample solution with the rate of 1.5 mL min^{-1} . A solution containing 1%(w/v) molybdenum and 1-10 mg L^{-1} of the analytes of interest was used for establishing the operating conditions. Gas-flow controllers were used for the outer (plasma), the carrier and the sheathing gas with flow-rates of 13, 0.40 and 0.30 L min^{-1} , respectively with the plasma operated at 1,000 W.

AAS. A Perkin-Elmer Model 3030B atomic absorption spectrometer was used for atomic absorption measurements. The selected instrumental parameters of element, wavelength (nm), spectral bandwidth (nm), and used gas are such that Al, 309.3, 0.7, $\text{C}_2\text{H}_2/\text{N}_2\text{O}$; Ba, 553.6, 0.4, $\text{C}_2\text{H}_2/\text{N}_2\text{O}$; Ca, 422.7, 0.7, $\text{C}_2\text{H}_2/\text{N}_2\text{O}$; Cd, 228.8, 0.7, $\text{C}_2\text{H}_2/\text{Air}$; Co, 240.7, 0.2, $\text{C}_2\text{H}_2/\text{Air}$; Cr, 357.9, 0.7, $\text{C}_2\text{H}_2/\text{Air}$; Cu, 324.8, 0.7, $\text{C}_2\text{H}_2/\text{Air}$; Fe, 248.3, 0.2, $\text{C}_2\text{H}_2/\text{Air}$; Li, 670.8, 1.4, $\text{C}_2\text{H}_2/\text{Air}$; Mg, 285.2, 0.7, $\text{C}_2\text{H}_2/\text{Air}$; Mn, 279.5, 0.7, $\text{C}_2\text{H}_2/\text{Air}$; Ni, 232.0, 0.2, $\text{C}_2\text{H}_2/\text{Air}$; Sr, 460.7, 0.4, $\text{C}_2\text{H}_2/\text{N}_2\text{O}$; Ti, 364.3, 0.2, $\text{C}_2\text{H}_2/\text{N}_2\text{O}$; Y, 410.2, 0.2, $\text{C}_2\text{H}_2/\text{N}_2\text{O}$; Zn, 213.9, 0.7, $\text{C}_2\text{H}_2/\text{Air}$, respectively. Other experimental conditions were selected to produce the highest signal to background ratios.

D.C. arc AES. For the determination of trace elements, a Jarrel-Ash model 70-000 system with a 3.4 m focal length monochromator with a ruled grating. The selected instrumental parameters of element, wavelength (nm) are such that Al, 308.216; Be, 313.042; Bi, 306.772; Ca, 317.933; Cd, 228.802; Co, 240.725; Cr, 284.325; Cu, 259.940; Fe, 299.443; Mg, 277.983; Mn, 259.373; Nb, 319.498; Ni, 301.200; Ta, 271.467; Ti, 334.941; V, 310.230; Zn, 330.259, respectively. The current and arcing period used for the elemental analysis were 10 A and 40 s, respectively. The analytical wavelength of Ag used for internal standard as 244.793 nm.

Samples and Reagents. The molybdenum metal powder and molybdenum trioxide used for real sample tests were supplied by the Korea Tungsten Company. Water was purified by a Milli-Q system. Concentrated hydrofluoric acid and nitric acid used were analytical reagent grade. Molybdenum metal powder (6 N grade, Johnson Matthey) and molyb-

denum trioxide (6 N grade, Johnson Matthey) were used to prepare for standard matrix solutions. Metal standard solutions for ICP measurements were prepared by diluting 1,000 ppm stock solutions obtained by Spex Industries, Inc. Internal standard and buffer material used for d.c. arc AES were silver chloride (Zeebac Inc., GR) and specpure graphite powder (Bay Carbon, spectrographic grade), respectively.

Sample Preparation. Molybdenum and related samples were dissolved in a mixture of high-purity hydrofluoric and nitric acids for measurements by ICP-AES and FAAS. Three mL of hydrofluoric acid and 3 mL of concentrated nitric acid were slowly added to 1 g of sample. The mixture was then heated in a microwave digestion system (CEM, MDS-81D) until dissolution was achieved. The dissolved solution was diluted with deionized water to give a final volume of 100 mL. For d.c. arc AES, molybdenum powders were converted into the trioxide by placing in a muffle furnace at $400 \pm 2^\circ\text{C}$ for 2 hours. Samples were mixed with buffer (2 parts sample+3 parts buffer) with Wig-L-Bug shaker for 60 s. The composition of buffer used was 1 part silver chloride (Zeebac Inc., GR) and 2 parts specpure graphite powder (Bay Carbon). The mixture of 75 mg was then loaded into graphite cups (Bay Carbon S-12). Trace element analysis was done with current of 10 A and arcing period of 40 s. The signal at 244.793 nm line of Ag was used for internal standard. Specpure molybdenum trioxide (Johnson Matthey) sparked with the analytes of interest was used to prepare the calibration standards.

Results and Discussion

Line Selection. Line selection was performed for 67 trace elements using a solution containing 10 g L^{-1} molybdenum. Spectral interferences of molybdenum lines on the 270 spectral lines of the elements were studied by scanning the molybdenum spectrum using the profiling mode of the analysis program. The various wavelengths for the elements found in this study are listed in Table 1. The wavelengths of the lines interfering on the lower wavelength and higher wavelength sides of the element lines are also given. Based on the present results the detailed information of this type on the spectral interferences allows the selection of wavelengths for the determination of particular element in molybdenum matrix prior to analysis. The best lines to analyze trace elements in molybdenum matrix to be suggested are Ag I 328.068, Al I 394.401, As I 228.812, Au I 242.795, B I 249.678, Ba II 455.403, Be II 313.042, Bi I 223.061, Ca II 393.367, Cd II 214.438, Ce II 413.765, Co II 228.616, Cr II 283.563, Cu I 327.396, Dy II 353.170, Er II 337.271, Eu II 412.970, Fe II 238.204, Ga I 294.364, Gd II 335.862, Ge I 219.871, Hf II 264.141, Hg I 253.652, Ho II 339.898, In I 451.131, Ir II 212.681, K I 766.490, La II 333.749, Li I 670.783, Lu II 219.554, Mg II 279.553, Mn II 257.610, Na I 588.995, Nb II 313.079, Nd II 406.109, Ni II 231.064, Pb II 220.353, Pd I 363.470, Pr II 417.939, Pt II 214.423, Rb I 780.023, Re II 227.525, Rh II 249.077, Ru II 240.272, S I 180.676, Sb I 217.584, Sc II 363.074, Se I 196.030, Si I 250.690, Sm II 442.434, Sn II 189.930, Sr II 407.771, Ta II 240.063, Tb II 350.917, Te I 214.281, Th II 283.231, Ti II 337.280, Tl I 276.787, Tm II 313.126, U II 385.958, V II 310.230, W II 209.475, Y II 377.433, Yb II 369.419, Zn I 213.856 and Zr II 349.621.

Table 1. Interference correction coefficients (K_{ij}) and spectral line interference inventory for trace element analysis in molybdenum matrix by ICP-AES^a

Analyte line	K_{ij}	Interferent lines	Analyte line	K_{ij}	Interferent lines
Ag I 328.068	0.032	328.119	C I 193.091		
I 338.289	0.216	338.279	I 247.856		247.822, .868
I 243.779	7.860	243.779, .848			
Al I 309.271	0.541	309.210, .259, .280	Ca II 393.367	0.003	
I 309.284	0.439	309.266	II 396.846	0.006	396.854, .867
I 394.401	0.217	394.305	II 317.933	0.311	317.933
I 396.152	16.51	396.148	I 422.673	0.285	422.715
As I 193.759	1.530	193.748, .756, .775	Cd II 214.438	0.013	214.408
I 197.262	9.646	197.225, .271, .278	I 228.802	0.040	228.802
I 200.334		200.284, .322, .384	II 226.502	0.074	226.478, .502
I 228.812	0.659	228.803, .874			
Au I 242.795	0.000	242.729, .812	Ce II 413.765	0.000	413.681, .821
I 267.595	0.023	267.604, .626, .645	II 413.380	0.000	
I 197.819	0.163	197.729, .838, .900	II 418.660	0.000	418.589, .636
II 208.209	3.837	208.175, .209, .252	II 393.109	0.311	393.077
B I 249.773	0.238	249.743, .834	Co II 228.616	0.025	228.643
I 249.678	0.185	249.638, .658, .708	II 238.892	0.045	238.872, .924
I 208.959	34.03	208.838, .959	II 237.862	0.222	237.865
I 208.893	1.711	208.843, .893	II 230.786	0.141	230.688, .800
			I 345.351	0.816	345.270, .342, .350
Ba II 455.403	0.003		Cr II 205.552	1.776	205.481, .561
II 493.409	0.004		II 206.149	0.048	206.164, .189
II 233.527	0.014	233.498, .489, .548	II 267.716	0.397	267.651, .682, .707
II 230.424	2.759	230.424	II 283.563	0.034	283.533, .560, .631
			II 284.325	0.046	284.293, .310, .375
Be I 313.042	0.003		Cu I 324.654	0.868	324.754
I 234.861	0.005	234.891	II 224.700	1.415	224.700
II 313.107	0.008		I 219.958	0.447	219.956
I 249.473	0.808	249.463	I 327.396	0.023	327.354, .455
Bi I 223.061	0.034	223.012, .120	Dy II 353.170	0.000	
I 306.772	23.65	306.742, .782	II 364.540	0.000	
I 222.825	1.148	222.786, .853	II 340.780	0.301	340.725, .761
I 206.170	3.543	206.180, .211	II 353.602	0.000	
Er II 337.271	0.000	337.304	In II 230.606	1.200	230.565, .585, .653
II 349.910	0.756	349.910	I 325.609	13.55	325.617
II 323.058	0.009	322.968, .024	I 451.131	0.000	451.080(Ar), 451.216
II 326.478	0.116	326.389, .448, .515	I 303.936	0.000	303.878, .903, .980
Eu II 381.967	0.023	381.913, .981	Ir II 224.268	0.197	224.220, .256, .280
II 412.970	0.000	413.010	II 212.681	0.000	212.644, .728
II 420.505	0.000	420.573	I 205.222	1.147	205.190, .214, .246
II 393.048	0.014	393.021, .072	II 215.268	1.014	215.247, .277, .332
Fe II 238.204	0.026	238.207, .230	K I 769.896	0.333	
II 239.562	0.193	239.524, .562, .600	I 766.490	0.080	
II 259.940	0.037	259.918, .956	I 404.414	9.318	404.414
II 234.349	0.076	234.300, .372			
Ga I 294.364	0.000	294.284, .335, .399	La II 333.749	0.000	
I 417.206	0.000	417.172, .225	II 379.478	0.000	379.446
I 287.424	0.000	287.365, .457, .483	II 408.672	0.000	408.605
I 403.298	0.000	403.251, .365	II 412.323	0.000	412.235, .365

Table 1. Continued.

Analyte line			K_{ij}	Interferent lines		Analyte line			K_{ij}	Interferent lines	
Gd	II	342.247	0.450	342.230,	342.275	Li	I	670.783	0.014		
	II	336.223	0.219	336.198,	336.256						
	II	335.047	0.219	335.033							
	II	335.862	0.000	335.814							
Ge	I	209.426	3.478	209.398,	429, 490	Lu	II	261.542	0.078	261.542,	.579
	I	265.118	0.134				II	291.139	0.091	291.090,	.191
	I	206.866	9.284	206.819,	.866, .887		II	219.554	0.000	219.490,	.533, .582
	I	219.871	0.052	219.808			II	307.760	5.846	307.717,	.763, .803
Hf	II	277.336	0.256	277.339,	.378	Mg	II	279.553	0.004		
	II	264.141	0.000	264.098,	.111, .160		II	280.270	0.006	280.237	
	II	232.247	3.054	232.247,	.294, .318		I	285.213	0.018		
	II	263.871	96.50	263.833,	.877		II	279.806	5.648	279.791,	.806
Hg	II	194.227	0.673	194.157,	.224, .284	Mn	II	257.610	0.005	257.581,	.655
	I	253.652	0.000	253.683			II	259.373	4.050	259.341,	.373
	I	184.890	0.307	184.833,	.858, .887		II	260.569	0.017	260.594	
					II		294.920	0.044	294.920		
Ho	II	345.600	0.138	345.614,	.636	Na	I	588.995	0.353		
	II	339.898	0.000				I	589.592	2.262	589.581	
	II	389.102	0.000	389.070,	.121						
	II	347.426	0.000	347.503							
Nb	II	309.418	0.208	309.460,	.415, .430	Re	II	197.252	0.550	197.213,	.252, .272
	II	316.340	0.166	316.391			II	221.426	12.96	221.406,	.426
	II	313.079	0.089	313.003,	.056		II	227.525	0.195	227.437,	.574
	II	269.706	0.261	269.685,	.72		II	189.777	1.620	189.747,	.777, .797
Nd	II	401.225	0.051	401.120		Rh	II	233.477	8.682	233.424,	.480, .488
	II	430.358	0.022	430.397			II	249.077	0.085	249.017,	.060
	II	406.109	0.000				I	343.489	5.744	343.478,	.541
	II	415.608	0.075	415.542			II	252.053	0.071	252.039,	.076
Ni	II	231.604	0.052	231.563,	.645	Ru	II	240.272	0.000	240.191,	.341, .353
	II	221.647	0.462	221.596,	.659		II	245.657	1.356	245.651	
	I	232.003	3.516	231.991,	232.006		II	267.876	0.382	267.845,	.876, .916
	II	216.556	0.205	216.511,	.580		II	269.206	0.491	269.160,	.179, .211
P	I	177.440				S	I	180.676	0.00	180.631,	.647, .718
	I	178.229		178.163,	.248, .303		I	181.978	1.412	181.959,	.981, .989
	I	213.618	22.23	213.554,	.606, .661		I	182.568	0.00	182.513,	.557, .595
	I	214.914	8.507	214.896,	.914, .975						
Pb	II	220.353	0.210	220.329,	.365	Sb	I	206.833	1.318	206.813,	.873
	I	216.999	1.739	217.014			I	217.584	0.412	217.544	
	I	261.418	0.486	261.371			I	231.147	2.299	231.137	
	I	283.306	1.400	283.327			I	252.852	1.950	252.842,	.882
Pd	I	340.844	1.013	340.436		Sc	II	361.383	0.018	361.435	
	I	363.470	0.000	363.521,	.455		II	357.252	0.103	357.252	
	II	229.651	0.089	229.587,	.627, .692		II	363.074	0.005		
	I	324.270	0.000	324.248,	.322		II	364.279	0.033		
Pr	II	390.844	1.299	390.860		Se	I	196.030	0.854	196.030,	.079
	II	414.311	0.062	414.357			I	203.985	5.569	203.985,	.004
	II	417.939	0.000								
	II	422.535	0.000	422.498							

Table 1. Continued.

Analyte line		K_{ij}	Interferent lines	Analyte line		K_{ij}	Interferent lines
Pt	II 214.423	0.026	214.405	Si	I 251.611	6.374	251.560, .608, .642
	II 203.646	1.656	203.621, .640, .677		I 212.412	19.35	212.330, .406, .482
	I 204.937	6.839	204.934, .952		I 288.158	0.282	288.141, .170, .193
	I 265.945	0.769	265.908, .954, .970		I 250.690	0.199	250.642, .667
Rb	I 780.023	0.00		Sm	II 359.260	0.164	350.260, 359.211
					II 442.434	0.000	Ar I 442.399, 442.367
					II 360.949	0.297	360.952
					II 363.429	0.00	Ar I 363.446, 363.509
Sn	II 189.930	0.639	189.910	U	II 385.958	0.000	
	I 235.484	0.847	235.474, .504		II 367.007	0.139	366.936, 367.067
	I 242.950	6.760	242.940, .950		II 263.553	21.85	263.490, .500, .528
	I 283.999	0.945	283.959, 284.009		II 409.014	0.000	408.972, 409.086
Sr	II 407.771	0.002		V	II 309.310	0.318	309.284, .299, .332
	II 421.552	0.002			II 310.230	0.171	310.236(OH)
	II 216.596	6.310	216.596		II 292.402	0.246	292.341, .434
	II 215.284	0.284	215.275, .287		II 290.882	0.180	290.866, .898, .911
Ta	II 226.230	0.342	226.197, .218, .272	W	II 207.911	1.139	207.890, .911, .929
	II 240.063	0.080	240.083		II 224.875	0.942	224.845, .878, .902
	II 268.517	0.970	268.517, .579, .837		II 218.935	60.27	218.881, .926, .986
	II 233.198	4.245	233.210, .266		II 209.475	0.908	209.429, .472, .493
	II 238.706	1.993	238.689, .706, .776				
Tb	II 350.917	0.000		Y	II 371.030	0.019	371.030
					II 324.228	0.016	
					II 360.073	0.037	
					II 377.433	0.005	
Te	I 214.281	0.572	214.251, .291	Yb	II 328.937	0.004	328.909, .985
					II 369.419	0.000	369.490, .337, .435
					II 289.138	1.905	289.099, .125, .164
	I 225.902	2.564	225.902, .951		II 222.446	0.091	222.395, .440, .467
					I 238.578	4.486	238.578, .608
Th	II 283.730	0.780	283.697, .730, .740	Zn	I 213.856	0.009	213.838
					II 202.548	0.136	202.588
					II 206.200	0.517	206.175, .200, .222
Ti	II 283.231	0.000	283.207, .267, .275	Zr	II 343.823	0.247	343.833
	II 274.716	4.000	274.692, .716, .740		II 339.198	0.628	339.188, .280
	II 401.913	0.000			II 257.139	1.980	257.139
					II 349.621	0.007	
Tm	II 334.940	0.041	334.891				
	II 336.121	0.512	336.135				
	II 323.451	0.032	323.379, .458, .505				
	II 337.280	0.010	337.305				
Tl	II 190.864	0.167	190.877, .905, .930				
	I 276.787	0.000	276.739, .758, .808				
	I 351.924	0.000					
	I 377.572	0.700	377.559, .607				
Tm	II 313.126	0.000					
	II 346.220	0.064	346.202, .294				
	II 384.802	0.034	384.729, .837				
	II 342.508	0.000	342.469, .516, .554				

* Gaps indicate no significant interferences. Wavelength units are in nm. The molybdenum concentration is 10 g L⁻¹.

Table 2. Recovery test for trace elements in molybdenum matrix by ICP-AES^a

Elements	Wavelength (nm)	spike	K_{ij} method		Matrix matching method
			K_{ij}	C_i^b	
Al	394.401	10.00	0.216	9.93	10.05
Ba	455.403	1.00	0.003	0.97	0.98
Be	313.042	1.00	0.003	0.96	1.02
Ca	393.367	1.00	0.003	0.94	0.95
Cd	214.438	1.00	0.013	1.02	0.98
Co	228.616	10.00	0.025	9.93	10.05
Cr	283.563	10.00	0.034	10.05	9.90
Cu	327.396	10.00	0.023	9.88	10.02
Fe	238.204	10.00	0.026	10.11	10.05
Li	670.783	1.00	0.014	1.08	0.97
Mg	279.553	1.00	0.004	1.03	1.02
Mn	257.610	1.00	0.005	1.04	0.95
Nb	313.079	10.00	0.089	10.16	10.04
Ni	231.604	10.00	0.052	10.10	9.92
Sc	363.074	1.00	0.005	0.99	1.04
Sr	407.771	1.00	0.003	1.03	0.95
Ta	240.063	10.00	0.080	10.12	10.06
Ti	337.280	10.00	0.010	10.12	10.00
V	310.230	10.00	0.171	10.13	10.10
Y	377.433	1.00	0.005	0.93	1.03
Zn	213.856	1.00	0.009	1.02	0.99
Zr	349.621	10.00	0.007	9.85	10.08

^aConcentrations are in ppm. The molybdenum concentration is 10 g L⁻¹. ^b C_i^b denotes corrected concentration. See text for the equations to calculate K_{ij} and C_i^b values.

Interference Correction Coefficient. For the simultaneous determination of trace elements in molybdenum the most sensitive lines for each element can not be always used due to the possible interferences of molybdenum lines. In order to quantitatively evaluate the amount of spectral interferences of molybdenum lines, interference correction coefficient (K_{ij}) for all of the 270 lines of the elements were calculated. The K_{ij} is defined by Eq. (1) and the values are listed in Table 1.

$$K_{ij} = \frac{\text{Spurious concentration observed for element } i \text{ (ng/mL)}}{\text{Actual concentration of interferent } j \text{ (}\mu\text{g/mL)}} \quad (1)$$

The K_{ij} value of 0.01 means that spurious concentration of 100 ppb was observed for the element i in the matrix solution of 1.00%(w/v). Therefore, it is recommended that the K_{ij} value be less than 0.01 in order to analyze trace element whose concentration is less than 10 ppm in the solid matrix. The elements which have less than 0.01 of K_{ij} value in the molybdenum matrix are found to be Au, Ba, Be, Ca, Ce, Dy, Er, Eu, Ga, Gd, Hf, Hg, Ho, In, Ir, La, Lu, Mg, Mn, Nd, Pd, Pr, Ru, Sc, Sm, Sr, Tb, Th, Ti, Tm, U, Y, Yb, Zn and Zr. The corrected concentrations using the K_{ij} values were calculated from Eq. (2).

$$C_i^b = C_i - K_{ij} C_j \quad (2)$$

Table 3. Comparison of limits of detection for multi-element analysis in molybdenum matrix by ICP-AES^a

Elements	Wavelength (nm)	K_{ij} method			FAAS ^d	d.c. arc AES ^e
		BEC ^b	RSD (%) ^c	LOD		
Al	394.401	3.096	1.18	109.	85.5	75.0
Ba	455.403	0.183	0.65	3.6	65.1	
Be	313.042	0.048	1.40	2.0		30.5
Bi	223.061	2.202	1.16	76.6		90.5
Ca	393.367	0.084	0.81	2.0	15.0	97.0
Cd	214.438	0.194	1.60	9.3	37.0	90.0
Co	228.616	0.418	1.55	19.4	80.5	70.5
Cr	284.325	0.632	1.45	27.5	65.0	50.9
Cu	327.396	0.576	0.93	16.1	57.0	48.3
Fe	238.204	0.377	1.38	15.6	40.0	55.0
Li	670.783	1.604	1.20	57.8	55.5	
Mg	279.553	0.043	2.40	3.1	10.0	50.0
Mn	257.610	0.063	3.10	5.7	20.5	35.5
Nb	313.079	1.697	0.54	27.2		500.5
Ni	231.604	0.789	0.60	14.2	70.5	65.0
Sc	363.075	0.205	0.41	2.5		
Sr	407.771	0.049	0.86	2.3	14.0	
Ta	240.063	1.260	0.96	36.1		520.0
Ti	337.280	0.498	0.53	7.8	65.0	60.0
V	290.882	1.977	0.93	54.9		95.0
Y	377.433	0.737	0.29	6.4	55.0	
Zn	213.856	0.154	1.50	6.9	55.5	90.5
Zr	349.621	0.273	0.73	5.9		

^aLimits of detection (LOD) are in ppb. The molybdenum concentration is 10 g L⁻¹. ^bBackground equivalent concentration in ppb. ^cRelative standard deviation of background signal. ^dSee text for the wavelengths used for these methods.

where C_i^b , C_i and C_j are corrected, measured and matrix concentration, respectively. The corrected concentrations thus should be more reliable data in the determination of trace elements in molybdenum matrix. The analytical reliability of the proposed method was estimated by analyzing spiked solutions prepared from ultrapure molybdenum metal. A solution containing 1 and 10 ppm each for 23 elements and 1% molybdenum was analyzed. The summary of analytical results are given in Table 2. The test solution was also analyzed using the matrix matching calibration technique. The data in Table 2 clearly indicate that the accuracy of multi-element analysis using the proposed technique is quite satisfactory.

Limit of Detection. The limits of detection (LOD) for 23 elements are listed in Table 3. The LOD given in Table 3 is defined as the concentration required to give a signal three fold greater than the standard deviation of the background fluctuation. The relative standard deviation of the background was determined in each selected analytical line for ten replicates measured with 0.5 s integration time. The average value of standard deviation is found to be about 1% for the molybdenum matrix solution. This value does not significantly differ from that found for pure water. On the other hand, the signal to background ratios were remarkably

decreased in the presence of matrix, which explains the difference between the LODs measured in water and with matrix. In comparison with LODs in aqueous solution, ICP-AES detection limits in a molybdenum concentration of 10 g L^{-1} were decreased by factors varying from 1 to 20. The values of LOD for the elements determined by the present technique are also compared with those obtained by AAS and d.c. arc AES in Table 3. The results indicate that the LODs for all of the elements determined by the proposed method are significantly better than those obtained by other techniques.

Analysis of Commercial Product. Trace element analysis of molybdenum powder, molybdenum trioxide samples obtained from the Korea Tungsten Company were performed by the K_{ij} correction method. For all of the samples, the elements listed in Table 2 except for Fe were found to be below the limit of detection. The concentrations of Fe found in molybdenum powder and molybdenum trioxide samples were measured to be 50.5 and $40.3 \mu\text{g g}^{-1}$, respectively. These data are in good agreement with those certified by the company. The samples were also analyzed by FAAS and d.c. arc AES. Except Fe the elements listed in Table 2 were not detected by these methods. In case of Fe the determined values for both of the samples also agreed with the certified values.

References

1. Bever, M. B. *Encyclopedia of Materials and Engineering*; MIT press: Boston, U.S.A., 1986; p 4159.
2. Kny, E.; Otner, H. M. *Int. J. Refract Hard Met.* 1985, 4(2), 77.
3. Henrion, G.; Gelbrecht, J.; Lippert, H. *Z. Chem.* 1980, 20(3), 108.
4. Mogi, F.; Itoh, K.; Okamoto, N.; Narita, M.; Fujine, M. *Denki Seiko* 1988, 59(4), 263.
5. Kujirai, O.; Yamada, K.; Kohri, M.; Okochi, H. *Fresenius' J. Anal. Chem.* 1991, 339(3), 133.
6. Mizota, T.; Nakmure, T.; Iwasaki, K. *Bunseki Kagaku* 1992, 41(9), 425.
7. Docekal, B.; Krivan, V. *J. Anal. At. Spectrom.* 1993, 8(4), 637.
8. Kujirai, O.; Yamada, K.; Kohri, M.; Okochi, H. *Anal. Sci.*, 7 (Suppl., Proc. Int. Congr. Anal. Sci., 1991, Pt. 1), 99.
9. Yamaguchi, H.; Kobayashi, T.; Yamada, K.; Okochi, H. *Bunseki Kagaku* 1990, 39(1), 19.
10. Yamaguchi, H.; Yamada, K.; Kujirai, O.; Hasegawa, R. *Bunseki Kagaku* 1993, 42(3), 145.
11. Ullmann, R.; Ringer, H. *Fresenius' Z. Anal. Chem.* 1986, 323(2), 139.
12. Brenner, I. B.; Erlich, S.; Vial, G.; McCormack, J.; Grosdaillon, P.; Asher, A. E. *J. Anal. At. Spectrom.* 1987, 2(6), 637.
13. Carre, M.; Diaz de Rodriguez, O.; Mermet, J. M.; Bridenne, M.; Marot, Y. *J. Anal. At. Spectrom.* 1991, 6(1), 49.