Determination of Molybdenum in Soil, Coal and Industrial Residue Samples by Flame Atomic Absorption Spectrometry

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This paper proposes a procedure for mineralization and determination of trace amounts of molybdenum in various solid samples. The samples including soil, coal and slag of power plants, furnace residue of the thermoelectric power plant and other industrial solid residues were collected from 8 different cities of Turkey. Molybdenum was extracted from matrices by conventional open wet digestion procedure. For this purpose, aqua regia was used as digestion solvent. Molybdenum concentrations in clear solution were determined by flame atomic absorption spectrometry. The determined Mo concentrations were found to be in range of 0.18 and 0.29 µg/g for soil, 4.9 and 54.6 µg/g for coal, 9.9 and 32 µg/g for power plants slag and 27.8-2295 µg/g for industrial residue samples. To establish the validity of the results, the recoveries from solid samples fortified with Mo were found to be at least 90 %. The effect of contamination was eliminated by subtracting the values obtained for blanks.

Key Words: Molybdenum, Industrial residue, Coal, Soil, Flame atomic absorption spectrometry.

INTRODUCTION

Molybdenum is an essential trace element for both plants and animals as well as for human being[1,2]. It is a component of many enzymes responsible for the initial stages of nitrogen, carbon and sulphur metabolism of plants, animals and human[3,4]. Its requirement for human is 25 µg per day, approximately, or possibly less and an intake of 150 µg per kg body weight may be toxic[5]. Thus, either a deficiency or an excess of Mo can cause the damage to plants, and its routine control is, therefore, highly important for healthy plant growth[6].

Molybdenum as a microelement is of great interest because high concentrations of Mo in soils, sediments and sludges, either from natural sources or through pollution, can enter the food chain through plant uptake, direct ingestion of soil by animals or through water supplies. As a result, strict control of Mo concentrations in environmental samples is necessary. Investigation of the sources of molybdenum in the geological matrices indicates an increased awareness of the potential exposure arising from environmental pollution[7].

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Owing to its properties such as high melting point, high strength at higher temperatures, good corrosion resistance and high thermal conductivity, Mo is widely used in a variety of industrial processes such as alloying agent in steels and cast iron, high-temperature alloys, tool steels, pigments for printing inks, paints and ceramics, catalyst, solid lubricants, missile and aircraft parts, reactor vessels, cements, die-casting copper base alloys and special batteries[1,7].

There are many analytical techniques available for the determination of Mo such as neutron activation analysis (NAA), inductively coupled plasma-mass spectrometry (ICP-MS), inductively coupled plasma-atomic emission spectrometry (ICP-AES), flame and flameless atomic absorption spectrometry (FAAS and ETAAS), voltammetry, spectrofluorimetry and spectrophotometry. Some of these techniques such as NAA and ICP-MS have high cost and necessitate the use of rather sophisticated. Relative to FAAS, flameless AAS has some disadvantages such as its high cost, slowness and greater proneness to interferences as well as its high sensitive advantage. On the other hand, it is recognized that FAAS should be preferred to flameless AAS if both of these methods can be applied for any sample due to some advantages of this method such as fast cheap and no need expert operators[8].

The mineralization of geological samples for determination of trace amounts of Mo has been performed using wet acid digestion. For this purpose, different acid mixtures were generally used. A procedure for the digestion of geological samples using aqua regia by refluxing has been described and this method has been particularly recommended for samples such as rocks, soils or sediments[7].

In this study, conventional open wet digestion procedure using aqua regia was chosen. The solid samples such as soil, slag and furnace residue were collected from different industrial and unpolluted sites in Yatagan, Elbistan, Diyarbakir, Sirnak, Batman, Hazro, Maden and Silopi cities in Turkey. For determinations, FAAS was used.

EXPERIMENTAL

An ATI UNICAM Model 929 flame atomic absorption spectrophometer (FAAS), equipped with ATI UNICAM hollow cathode lamp and deuterium background correction were used for molybdenum determinations. The optimum conditions for FAAS are given in Table-1. The other apparatus used were magnetic stirrer (Velp Scienttifica) and centrifuge (Heittich EBA III).

TABLE-1
OPERATING PARAMETERS FOR MOLYBDENUM DETERMINATION BY FAAS

Parameters	Mo	Parameters	Mo
Wavelength (nm)	313.3	Slit width (nm)	0.5
HCl current (mA)	10	C_2H_2 flow rate (L/min)	4.2
Type of flame	C_2H_2–N_2O	N_2O flow rate (L/min)	4.7
Background correction	Deuterium lamp	–	–

Unless stated otherwise, all chemicals (Merck) used were of analytical-reagent grade. Throughout all analytical work, double distilled water was used. All pyrex glassware was kept permanently full of 1 M nitric acid when not in use. In digestion procedure, aqua regia was used. Stock standard Mo solution of 1000 mg/L was prepared by dissolving $(NH_4) Mo_7O_{24}.4H_2O$ in diluted (1/20) aqua regia.

Preparation of samples: The samples including soil, coal and slag of power plants, furnace residue of the thermoelectric power plant and other industrial solid residues were collected from Yatagan, Elbistan, Diyarbakir, Sirnak, Batman, Hazro, Maden and Silopi, Turkey. The soil samples were taken with the sampling at a depth of about 10 cm below the surface. Then, *ca.* 500 g of soil was put into a poly-ethylene container and transferred into laboratory. The samples were dried at 100 ºC in an oven and subsequently grinded in a porcelain mortar and sieved from 100 mesh (Tylor). Samples of 0.10-5.00 g were placed into a pyrex flask and digested by adding 5 mL of aqua regia. For this purpose, the mixture was heated by occasionally stirring on a hot plate near to dryness. This process was repeated. Finally, the residue was dissolved in 3 mL of diluted aqua regia (1/20). After centrifugation, the clear solution was analyzed by FAAS. A blank digest was carried out in the same way. Four sub-samples of each sample were treated by the same digestion procedure.

Calibration: In order to overcome the probable enhancement or suppression due to the presence of matrix components, the calibrations were performed within the sample matrix itself. As a result, the solutions for calibration graphs were contained matrix components at the following concentrations (as µg/mL); Ca^{2+}: 5000, Mg^{2+}: 500, Al^{3+}:100, Fe^{3+}: 50, Cl^- and SO_4^{2-}: 200 and PO_4^{3-}: 100. These solutions were referred as model solutions.

Direct calibration curve was obtained using the molybdenum solutions from 1.0 to 10 µg/mL including model solutions described above. The solutions were prepared both in diluted (1/20) aqua regia and in 1 M of nitric acid, separately. The graphs obtained were rectilinear in the concentration range of described above and the equations of the curves were as follows:

$$Y = 27.94x - 3.8 \qquad R^2 = 0.999 \text{ (in diluted 1/20 aqua regia)}$$

$$Y = 4.497x - 1.5 \qquad R^2 = 0.996 \text{ (in 1 M of nitric acid)}$$

The difference in the slopes of equations may be attributed to the formation thermally stable oxide compounds such as MoO_2, MoO_3 and Mo_4O_{11} in spite of using N_2O/C_2H_2 flame. The formation of these compounds can be hindered in aqua regia medium. Consequently, calibration solutions prepared in diluted aqua regia (1/20) medium were used in subsequent studies due to high sensitivity of Mo in this medium.

RESULTS AND DISCUSSION

Analytical performance: The accuracy of the method was studied by examining the recoveries from solid samples fortified with various amounts of molybdenum. The following Mo amounts considering its concentrations in the samples were added: 0.3 µg/g for soil of Diyarbakir Hevsel Gardens, 20 µg/g for slag of Yatagan Power Plant, 50 µg/g for Silopi coal and 2500 µg/g for stove residue of Sirnak coal. After digestion as mentioned in experimental section, the recoveries were found to be at least 90 % for all studied samples. The effect of contamination was eliminated by subtracting the values obtained for blanks. Adsorption losses can be excluded as the procedure was followed in exactly the same way, using the same glassware and the same reagents throughout the work. The results showed that there were no contamination or adsorption losses at the studied conditions.

Level of molybdenum in the reagent blank in total analytical steps was found to be 75 ng/mL with standard deviation of 11. Therefore, the detection limit for molybdenum, defined as three times the s value of blank was calculated as 33 ng/mL. The standard deviation for 10 replications of the same sample was found to be less than 10 %.

Applications: Molybdenum is a trace element in the earth's crust and the estimated abundance is in the range of 0.05-40 µg/g with a mean value of 1.5 µg/g [9]. Its levels in soils in various countries range from 0.034 to 2.9 µg/g (Table-2).

TABLE-2
REPORTED MOLYBDENUM CONCENTRATION IN VARIOUS
TERRITORY NATURAL SOILS

Soil sample and country	Concentration (µg/g)	Ref.
Soil (Spain)	1.050	10
Soil (India)	2.550	11
Soil (Red laterite soil, India)	2.900	12
Soil (Yellow soil, India)	2.400	12
Soil (Yellow-gray soil, India)	1.300	12
Soil (Gray soil, India)	0.800	12
Soil (Yellow soil, India)	1.400	12
Soil (Red laterite soil, India)	2.100	12
Soil (Spain)	0.235	13
Soil (Spain)	0.034	14
Soil (China)	1.920	15
Uncultivated soil: 10–20 cm (Greece)	0.900	16

The higher Mo contents were reported for rocks (1.12-4.8 µg/g) and for soil (0.034-43 µg/g)[9]. On the other hand, low Mo concentration (0.031-0.235 µg/g) has been reported in the soils of Spain by Molina-Diaz *et al.*[13] and Lunar *et al.*[14]. In the present study, Mo levels were found to be 0.18 and 0.29 µg/g in soil samples (Table-3).

The Mo content *in situ* coal is 30-32 which is higher compared to values reported on a worldwide scale[17]. Finkelman[18] suggested that Mo in coal is associated with

sulphides or organics. Molybdenum contents in the different selected coals were determined in range of 1.2-5.3 μg/g by Querol et al.[19]. Wagner et al.[20] reported Mo values in range of < 0.24-4.3 μg/g for selected Highveld coals. Mo concentration in worldwide coals is in range of 0.1-10 μg/g as well as its concentration in ranges of 3-7.5 and < 2-1.5 μg/g in US and British coals, respectively[17,21]. Its mean level in Australian coals is 1.5 μg/g[21]. Karayigit et al.[22] determined Mo levels in feed Turkish coal-fired plants from 3.0 to 129.0 μg/g. In the current study, the observed Mo level in Silopi coal (54.6 μg/g) was found to be at least 5-fold higher than in the world-wide coals[17], but Mo concentration in Hazro coal (4.9 μg/g) agree with Mo concentrations in worldwide coals.

TABLE-3
CONCENTRATIONS OF MOLYBDENUM IN VARIOUS SOLID
SAMPLES BY FAAS (On Dry WEIGHT BASIS, n = 4)

Sample	Concentration (μg/g) ± Standard deviation
Slag of Yatagan power plant	32.000 ± 1.90
Slag of Elbistan power plant	9.900 ± 0.16
Stove residue of Sirnak coal	2.295 ± 108.0
Silopi coal	54.600 ± 7.40
Diyarbakir-Hazro coal	4.900 ± 0.40
Dusts of inner walls of Elbistan power plant	29.200 ± 1.26
Soil (Batman-Tupras)	0.180 ± 0.03
Soil (Diyarbakir Hevsel Gardens)	0.290 ± 0.03
Flotation residue of Maden copper plant	27.800 ± 3.75

As it can be seen from Table-3, Mo concentrations range from 0.18 to 2.295 μg/g for the studied solid samples. Mo levels were found to be 9.9-32 μg/g in slag and 27.8-2.295 μg/g in the other solid industrial residue samples. The lowest level is for soil taken from Batman-Tupras and the highest level is for stove residue of Sirnak coal.

Conclusion

This paper proposes the determination of trace Mo in industrial residues and natural soils using aqua regia in conventional open wet digestion procedure. For determinations, FAAS is used. In some coals, Mo levels were found to be higher than in the worldwide levels, but in some coal samples, Mo concentrations agree with worldwide levels. Its levels were found to be rather high in the industrial residue solid samples (up to 2.295 μg/g). The validity of the procedure was confirmed by the recoveries at least 90 %. Consequently, the decomposition and determination procedures can also be used for different solid samples such as rocks, industrial residues, coals, fly ashes, ores and others.

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