
Chapter – 6

SPECTROPHOTOMETRIC DETERMINATION OF MOLYBDENUM(VI)

Introduction

The chemistry of molybdenum is very complex in nature. The compounds containing molybdenum in 0, +2, +3, +4, +5 and +6 oxidation states are known to exist. Molybdenum occurs principally in +6 oxidation state as molybdate (MoO_4^{2-}) ions, which forms condensed species in acid media. In acidic solutions, molybdenum exists as molybdenyl cation MoO_2^{2+} . Depending on the reducing agent used and on the reduction conditions. Mo (VI) is reduced to Mo (V) or Mo (III). Molybdenum is obtained principally from the ore molybdenite (MoS_2). About 85% of molybdenum that is being produced is used in the manufacture of iron-based alloys. Molybdenum is also recovered as a byproduct of copper and tungsten mining operations. Molybdenum is added to the cast iron to increase its strength, which is widely used in the manufacture of automobile engines. Cast iron containing 3% of molybdenum withstands abrasive environment. Because of its contribution to increase the strength of iron, molybdenum is used in the manufacture of turbines and blades of jet engines. Because of the properties such as strength, stiffness, electrical and thermal conductivity and corrosion resistance, the alloys of molybdenum find numerous applications.

Molybdenum is being used as a catalyst in many petroleum and chemical processes. It is also used as activator or promoter of other catalysts. Purified molybdenum sulphide is an important dry lubricant. Zinc molybdates show an exceptional stability and anti-corrosion property. By adding molybdenum in the form of fertilizer, large increase in the crops yield, particularly of leguminus have been observed. The metal is also used in nuclear energy applications and for missile and aircraft parts. It is added in trace amounts in vitamin supplements and specialised medicines. Recent studies have shown that molybdenum is an important element in promoting healthy teeth.

Molybdenum is an essential trace element required by both plants and animals¹. Its biological role is extremely important in the nitrogen metabolism of plants. It is necessary for the reduction of nitrates for protein synthesis in all plants and for nitrogen fixation in the root modules of leguminous plants by Rhizobia bacteria. Molybdenum is harmful to both plants and animals at higher concentrations² ($>5 \mu\text{g g}^{-1}$) but soil that has no molybdenum at all cannot support plant life. Therefore its routine control is highly recommended for healthy plant growth. Molybdenum is added in trace amounts to fertilizers to stimulate plant growth.

Many spectrophotometric methods for the determination of molybdenum (VI) based on its reaction with thiocyanate in the presence of a reducing agent³ and with toluene-3, 4-dithiol⁴, are not too selective, because they are subject to interference from many other elements. Some of the recently proposed methods using thiosemicarbazones⁵ are found to be less sensitive. The methods employing different organic reagents have also been reported⁶. Although several methods have been reported for the spectrophotometric determination of Mo (VI)⁷⁻⁹, they suffer from drawbacks such as lack of reproducibility, stability, interferences and requirement of prior extraction. Table 6.1 comprises different spectrophotometric methods recently developed for the determination of molybdenum. In the present study, the investigator reports simple, sensitive and non-extractive spectrophotometric method for the determination of molybdenum in trace quantities using 2-AAINH.

Present investigations

Molybdenum (VI) forms a yellow coloured water soluble complex with 2-aminoacetophenone isonicotinoylhydrazone in acidic pH solutions. The colour formation is instantaneous and is stable for more than 48 hours.

Table 6.1
Analytical results of various spectrophotometric methods for Molybdenum

| Reagent used | λ_{\max} (nm) | pH | $\epsilon \times 10^4$ ($l \text{ mol}^{-1} \text{ cm}^{-1}$) | Beer's law range ($\mu\text{g mL}^{-1}$) | Remarks | Ref. No |
|---|--------------------------|---------|--|--|---|------------|
| Mendelohydroxamic acid | 375 | - | 1.62 | - | - | 10 |
| Heterocyclic dithio phosphate | 514 | Acidic | 0.38 | 5-110 | - | 11 |
| P-Diethyl amino phenyl fluorone- cetyl-pyridinium bromide | 532 | 2.8 | 11 | 0- | - | 12 |
| Quinalizann and cetyl pyridinium chloride | 580 | 3.2-4.2 | 12 | 0.05-0.6 | - | 13 |
| 3,5-dibromo-4-hydroxy phenyl fluorone | 530 | - | 13.5 | 0-0.6 | - | 14 |
| N-Hydroxy-N-p-chlorophenyl-o- chlorobenzamidine hydrochloride and thiocyanate | 470 | - | 0.33 | 3-24 | Extraction of ternary complex into benzene; low sensitivity | 15 |
| Alizarin red S in presence of a polymer | 500 | - | 2.1 | 0.05-5.5 | Cu(II), Al(III) and Fe(III) seriously inferred | 16 |
| Rhodamine 6G and thiocyanate | 570 | - | 11 | - | Required heating at 90°C for 10 min | 17 |
| Bromopyrogallol red | 634 | - | 6.0 | 0-0.8 | Collection and elution as molybdate ion on protonated chitin | 18 |
| 2,2'-Biquinoxalyl | 685 | - | 3.3 | 0.2-2.0 | Fe(III) and Cr(III) interfered seriously | 19 |
| 7,8-Dihydroxy-4-methylcoumarin and cetyltrimethylammonium bromide | 400 | 5.6-6.0 | 13.2 | - | Zr(IV) and W(VI) interfered | 20 |

Table 6.1 (Continued)

| Reagent used | λ_{\max} (nm) | pH | $\epsilon \times 10^4$ (l mol ⁻¹ cm ⁻¹) | Beer's law range ($\mu\text{g mL}^{-1}$) | Remarks | Ref. No |
|---|--------------------------|------------|---|--|--|------------|
| Malachite green and p-chloromandelic acid | 630 | 2.0-4.0 | 10.6 | 0.01-0.4 | Extraction into chlorobenzene | 21 |
| Acetonethiosemicarbazone and thiocyanate | 472 | - | 1.9 | 0.4-9.0 | Extraction of orange red ternary complex into chloroform | 22 |
| Gallic acid and hydroxylamine | 420 | - | 0.48 | 3.02-25.12 | Low molar absorptivity | 23 |
| 2-(2'-Furyl)-3-hydroxychromone | 414 | - | 5.18 | 0-2.7 | Many ions interfered | 24 |
| 3-Hydroxy-2-(4-methoxyphenyl)-6-methyl-4H-chromon-4-one | 411 | - | 5.61 | 0-2.3 | Suffered from interferences of common ions | 25 |
| Phenylfluorone and lauryl dimethylbenzylammoniumbromide | 526 | - | 10.5 | 0.02-0.14 | Low selectivity | 26 |
| Catechol violet in the presence of gelatin | 670 | - | 3.0 | 1.84-3.36 | Commonly associated metal ions and anions interfered | 27 |
| N-Phenylbenzohydroxamic acid | 395 | - | 0.32 | 0.9-45 | Low molar absorptivity | 28 |
| 1-Nitroso-2-naphthol | 380 | - | 0.25 | - | Low sensitivity | 29 |
| Thiocarbohydrazide derivatives | 380 | - | 0.66-0.84 | 1-15, 0.5-1.4 | Low molar absorptivity | 30 |
| Charge transfer complex | 660 | PVA medium | 1.47 | - | The proposed method had been applied to the determination of trace molybdenum in tungstan ore. | 31 |

Table 6.1 (Continued)

| Reagent used | λ_{\max} (nm) | pH | $\epsilon \times 10^4$ (l mol ⁻¹ cm ⁻¹) | Beer's law range ($\mu\text{g mL}^{-1}$) | Remarks | Ref. No |
|--|--------------------------|-------------------|---|--|--|------------|
| Charge transfer complex sensitized by copper (II) | 660 | - | 49.2 | 2.0-32.0 | The proposed method had been applied to the determination of trace molybdenum in tungstan ore. | 32 |
| Sodium Isoamyl Xanthate | 470 | 5M HCl (2ml) | 1.13 | 3.5-8.0 | The proposed method to applied for the determination of Mo(VI) in steel samples. | 33 |
| Polyphenols and thiazolyl blue | | Aqueous medium | - | - | The proposed method has been developed for determination Mo(VI) in products from ferrous metallurgy. | 34 |
| 9-(2,4-dihydroxy phenyl) -2,3,7-trihydroxyl-6-fluorone | 523 | - | 11.4 | - | The proposed method is applied for determination of trace Mo(VI) in plant tissues. | 35 |
| N,N'-bis(2-hydroxy-5-bromo-benzyl)1,2 diaminopropane | 342 | - | 9.6 | 0.0-9.9 | - | 36 |
| Salicylaldehyde Acetoacetic Acid Hydrazone | 470 | 1.0 | 1.6 | 0.097-0.968 | The proposed method is applied for determination of trace Mo(VI) in alloy samples | 37 |
| 4-Hydroxybenzaldehyde thiosemicarbazone | 365 | 6.0 | 1.25 | 0.03837-0.3837 | The proposed method is applied for determination of trace Mo(VI) in alloy samples | 38 |

Table 6.1 (Continued)

| Reagent used | λ_{\max} (nm) | pH | $\epsilon \times 10^4$ (l mol ⁻¹ cm ⁻¹) | Beer's law range ($\mu\text{g mL}^{-1}$) | Remarks | Ref. No |
|--|--------------------------|----------------|---|--|---|-------------------|
| cinnamaldehyde-4-hydroxy benzoylhydrazone (CHBH) | 404 | 3.0 | 6.82 | 0.047- 0.479 | The proposed method is applied for determination of trace Mo(VI) in alloy samples, food stuffs and pharmaceutical samples | 39 |
| 2-Hydroxy-3-methoxy benzaldehyde thiosemicarbazone (HMBATSC). | 375 | 1.5 | 2.47 | 0.24-4.32 | The proposed method is applied for determination of trace Mo(VI) in alloy samples and food stuffs | 40 |
| cetyl trimethyl ammonium bromide | 460 | extractio n | 4.01 | 0.1-4.2 | The proposed method is applied for determination of trace Mo(VI) in biological and environmental samples, including different types of water samples. | 41 |
| 2-Hydroxy-4-Chloro-5-Methyl Acetophenon Oxime (HCMAOX) | 410 | 3.0 | - | 6.1-4.4 | - | 42 |
| 2-Amino Acetophenone Isonicotinoyl Hydrazone | 385 | 3.0 | 1.21 | 0.49-7.34 | - | Present Method |

Section i : Zero order spectrophotometric determination of Molybdenum (VI)

a. Absorption spectra of 2-AAINH and the molybdenum (VI) complex in solution

The absorption spectra of the solution containing molybdenum (VI) yellow coloured complex [Mo(VI) – 2-AAINH] against the reagent blank and that of the reagent solution against the corresponding buffer blank were recorded in the wavelength region 350-500nm by adopting the procedure described in 3a. Typical spectra are presented in Fig. 6.i.1. The spectra show that molybdenum (VI) complex has an absorption maximum at 385 nm. However, at this wavelength, the reagent shows considerable absorbance. At 385 nm, the complex shows large absorbance while the reagent blank shows negligible absorbance. Hence, the analytical studies were carried out at 385 nm.

b. Effect of pH on the absorbance of the complex solution

The study (according to general procedure 3b) of the effect of pH on the colour intensity of the reaction mixture showed that the maximum colour was obtained in the pH range 2.5-3.5. Analytical studies were therefore, carried out at pH 3.0 (Fig. 6.i.2).

c. Effect of 2-AAINH concentration

The studies using the procedure 3c revealed that a 15 fold molar excess of 2-AAINH was essential for complete and constant colour development. The results are presented in Table 6.i.1.

d. Time stability of the coloured solution

The absorbance of the solution was measured at different time intervals to ascertain the time stability of the colour of the complex as described in 3d. The colour reaction between Mo (VI) and 2-AAINH was found to be instantaneous at room temperature and the colour remained stable for more than 48 hours.

TABLE 6.i.1
Effect of 2-AAINH concentration

$$\text{Mo (VI)} = 5 \times 10^{-5} \text{ M}$$

$$\text{pH} = 3.0$$

$$\text{Wave length} = 385\text{nm}$$

| [Mo(VI)] : [2-AAINH] | Absorbance |
|----------------------|------------|
| 1:5 | 0.325 |
| 1:10 | 0.482 |
| 1:15 | 0.692 |
| 1:20 | 0.582 |
| 1:25 | 0.434 |
| 1:30 | 0.425 |

e. Applicability of Beer's law

For the possible determination of molybdenum (VI) at micro levels, the absorbance of the solutions containing different amounts of metal ion was measured by adopting the procedure 3e. Calibration plot drawn between absorbance and amount of Mo (VI) (Fig. 6.i.3), showed that Beer's law was obeyed in the concentration range $0.49 - 7.34 \mu\text{g mL}^{-1}$ of Mo (VI). The straight line obeyed the equation $A = 0.1215C + 0.0308$. The molar absorptivity and Sandell's sensitivity were $1.21 \times 10^4 \text{ lit mol}^{-1}\text{cm}^{-1}$ and $0.008 \mu\text{g cm}^{-2}$ respectively.

Statistical analysis of results

The experimental data was treated with different statistical methods and the results are presented in Table 6.i.2.

The results in the Table 6.i.2 confirm the validity and reproducibility of the present method.

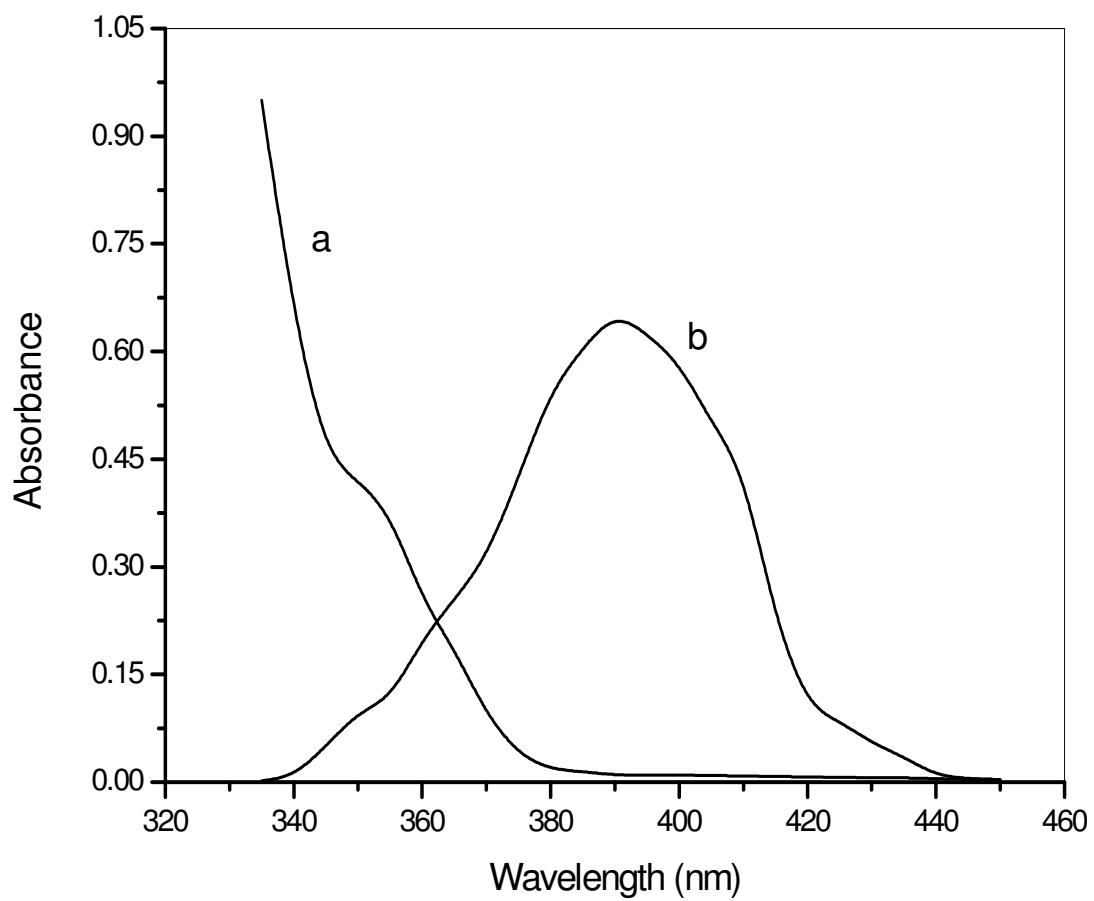


Fig. 6.i.1. Absorption spectra of
(a) 2-AAINH Vs Buffer blank
(b) [Mo(VI)-2-AAINH] Vs reagent blank
[Mo(VI)] = 5×10^{-5} M ; [AAINH] = 1×10^{-3} M ; pH = 3.0

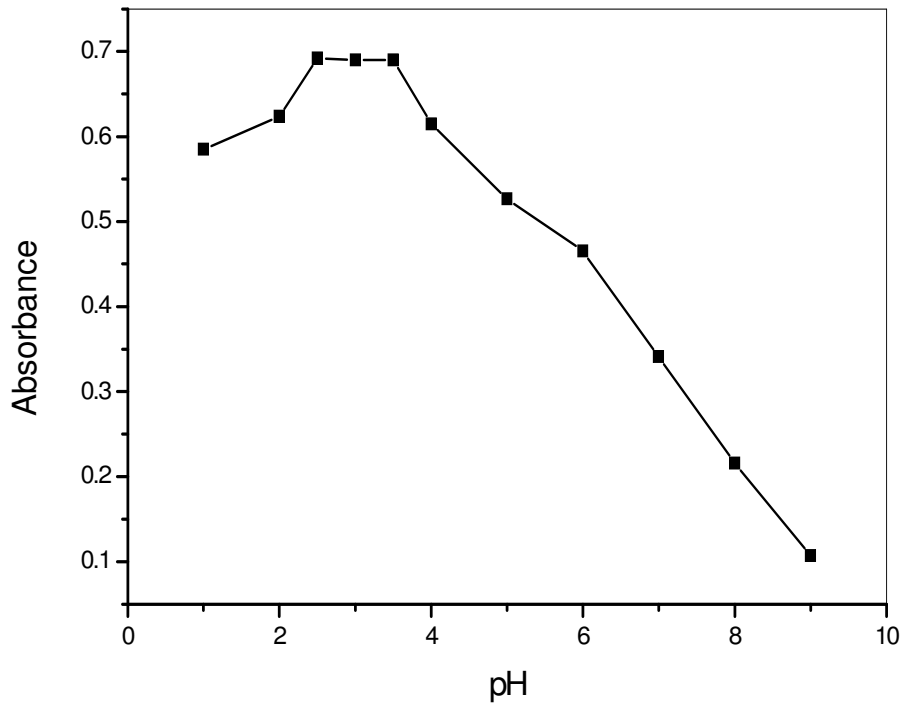


Fig. 6.i.2. Effect of pH on absorbance of Mo(VI) – 2-AAINH
 $[\text{Mo(VI)}] = 5 \times 10^{-5} \text{ M}$; $[\text{2-AAINH}] = 1 \times 10^{-3} \text{ M}$
 Wavelength = 385nm

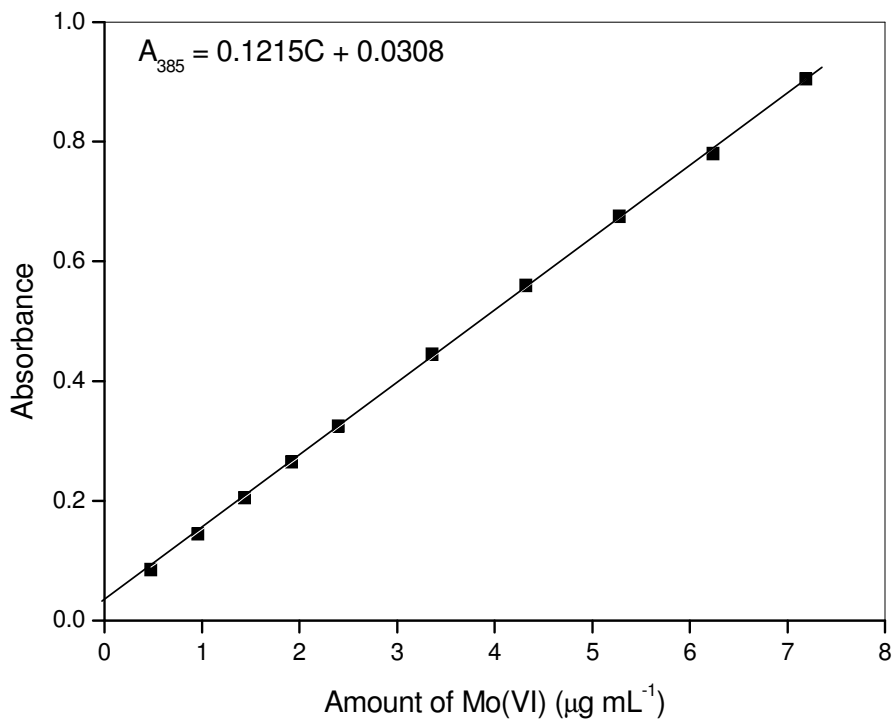


Fig. 6.i.3. Calibration plot
 $[\text{2-AAINH}] = 1 \times 10^{-3} \text{ M}$
 Wavelength = 385nm
 pH = 3.0

Table 6.i.2
Statistical analysis for the experimental data

| Parameter | Mo(VI) – 2-AAINH |
|-----------------------------|------------------|
| Angular coefficient (m) | 0.1215 |
| Y-Intercept (b) | 0.0308 |
| Correlation coefficient (r) | 0.9994 |
| Standard deviation (s) | ±0.0012 |

f. Effect of diverse ions

The effect of several diverse ions on the determination of Mo (VI) was examined under the optimum conditions (according to general procedure 3f). The extent of interference by various anions and cations was determined by measuring the absorbance of solutions containing a constant amount of Mo (VI) and varying amounts of diverse ions. The results are presented in Table.6.i.3.

The results in the table 6.i.3 reveal that majority of metal and non-metal ions do not interfere in the present method even in more than 100-fold excess. Pd (II), Fe(II), Ni (II), Co II), Mn (II) and V (V) are tolerable in 30-fold excess. Ru (III), Pt(IV), and Cu (II) interfere when present in five fold excess. However, in the presence of 1520 µg of ascorbic acid Ru (III) and Pt (IV) are tolerable up to 100-fold excess and in presence of 1330 µg of citrate, Cu (II) do not interfere even when present in 100-fold excess. Hence, the method can be fairly selective method.

Composition and stability of the complex

The composition of the complex was determined using the Job's and molar ratio methods.

Table 6.i.3**Tolerance limits of diverse ions**Amount of Mo (VI) = 1.965 $\mu\text{g mL}^{-1}$

| Diverse ion | Tolerance limit ($\mu\text{g mL}^{-1}$) | Diverse ion | Tolerance limit ($\mu\text{g mL}^{-1}$) |
|--------------------|---|--------------------|---|
| Ascorbic acid | 1520 | U(VI) | 867 |
| Citrate | 1330 | Te(IV) | 672 |
| Tartrate | 1245 | W (VI) | 593 |
| EDTA | 890 | Zr (IV) | 522 |
| Thiourea | 870 | Ti (IV) | 510 |
| Bromide | 800 | K (I) | 473 |
| Urea | 765 | Na (I) | 412 |
| Hypo | 715 | Th (IV) | 325 |
| Sulphate | 683 | Cd (II) | 311 |
| Iodide | 631 | Li (I) | 299 |
| Nitrate | 612 | Mg(II) | 275 |
| Acetate | 588 | Al (III) | 223 |
| Thiosulphate | 521 | Cr (III) | 210 |
| Phosphate | 472 | Ru (III) | 15,190 ^a |
| Fluoride | 454 | Pb (II) | 185 |
| Formate | 411 | Pt (IV) | 10,172 ^a |
| Chloride | 316 | Ce (IV) | 144 |
| Oxalate | 245 | Cu (II) | 12,111 ^b |
| | | Pd (II) | 55 |
| | | Fe (II) | 44 |
| | | Ni (II) | 44 |
| | | Co (II) | 35 |
| | | Mn (II) | 35 |
| | | V (V) | 30 |

In the presence of a) 1520 μg of ascorbic acid; b) 1330 μg of Citrate

g. Job's method

Job's curve shown in Fig. 6.i.4 indicates a composition of 1:1 for the complex. The stability constant of the complex was determined by Job's method as 4.44694×10^6 (according to general procedure 3g).

h. Mole ratio method

Mole ratio plot shown in Fig. 6.i.5 confirms the 1:1 composition of the complex between Mo (VI) and 2-AAINH (according to general procedure 3h).

Applications

The method proposed in the present studies was applied for the determination of molybdenum (VI) in food stuffs and in some alloy steels.

Application to food stuffs

The sample solutions were prepared by using the procedure 3u. The amount of molybdenum present in these samples was computed from a pre-determined calibration plot and the results are presented in Table 6.i.4.

Table 6.i.4
Determination of molybdenum in food stuffs

| Sample | Amount of molybdenum ($\mu\text{g mL}^{-1}$) | | Recovery (%) |
|---------|--|-----------------|--------------|
| | Standard method ⁴³ | Present method* | |
| Banana | 0.479 | 0.477 | 99 |
| Apple | 0.239 | 0.242 | 101 |
| Cabbage | 1.439 | 1.431 | 99 |
| Tomato | 0.959 | 0.971 | 101 |
| Rice | 0.718 | 0.714 | 99 |
| Potato | 0.240 | 0.234 | 97 |

* Average of five determinations.

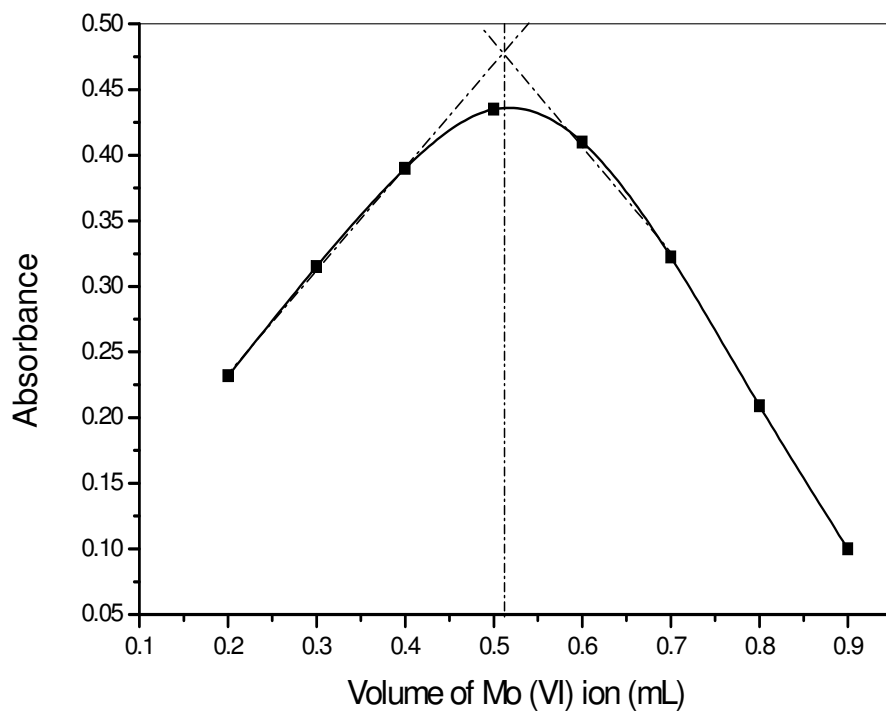


Fig. 6.i.4. Job's curve
 $[\text{Mo(VI)}] = [2\text{-AAINH}] = 1 \times 10^{-3}\text{M}$
 Wavelength = 385nm ; pH = 3.0

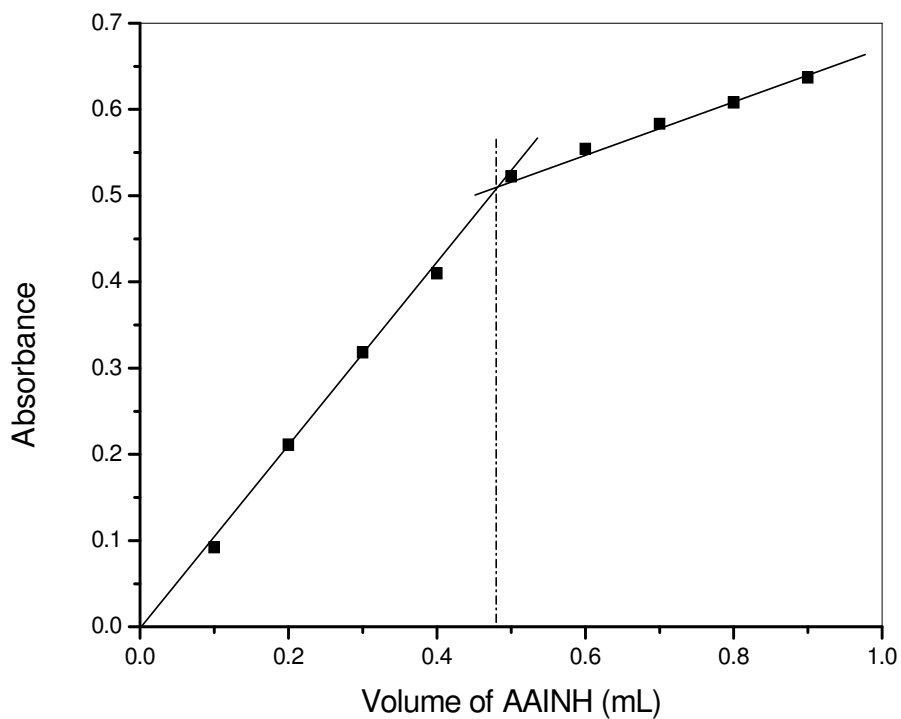


Fig. 6.i.5. Molar ratio plot
 $[\text{Mo(VI)}] = [2\text{-AAINH}] = 1 \times 10^{-3}\text{M}$
 Wavelength = 385nm ; pH = 3.0

Application to alloy steels

The sample solutions were prepared as described under general procedure 3(1).

The amount of Mo (VI) present was determined by the following procedure.

Procedure

A suitable aliquot of the sample solution was taken in a 10 ml standard flask containing 5ml of buffer of pH 3.0, 1330 µg of Citrate (to mask Cu) and 1ml of (1×10^{-2} M) 2-AAINH solution. The contents were diluted to 10 ml with distilled water and its absorbance was measured at 385 nm against the reagent blank. The absorbance values were referred to the pre-determined calibration plot to compute the amount of molybdenum present. The results are presented in Table 6.i.5.

Table 6.i.5
Determination of molybdenum in steels

| Sample | Compositions (%) | Amount of Mo (%) | | Relative error (%) |
|-----------|---|------------------|--------|--------------------|
| | | Certified | Found* | |
| BCS 406/1 | Mn(0.066); Cr(1.06); Mo(0.05); Ni (0.14); Co(0.016); Cu (0.09); V(0.19) | 0.050 | 0.052 | +4.00 |
| BCS 406 | Mn(0.53); Ni(1.69); Mo(1.03); V(0.02); Cr(2.12); Cu ^a (0.32) | 1.030 | 1.042 | +1.165 |
| BCS 219/4 | Mn(0.81); Cr(0.66); Mo(0.58); Ni(2.55); Cu ^a (0.088); Sn (0.011); Fe(95.0) | 0.580 | 0.574 | -1.032 |
| BCS 483 | W(10.8); Cr(3.21); V(0.54); Mn (0.29); Mo(0.17); Co(1.94); Rest Fe. | 0.170 | 0.166 | -2.354 |

* Average of five determinations.

a = masked with 1330 µg of Citrate

Section ii : Derivative spectrophotometric determination of Molybdenum (VI)

Molybdenum (VI) forms yellow coloured complex with 2-Amino acetophenone Isonicotinoyl hydrazone (2-AAINH). An attempt was made to develop derivative spectrophotometric (1st and 2nd) methods for the determination of molybdenum (VI) in micro amounts. The results are presented in this section.

Derivative spectra

The first and second derivative spectra of molybdenum (VI)-2-AAINH complex were recorded by the procedure described in 3i and was shown in Figs. 6.ii.1 and 6.ii.3 respectively.

The first derivative spectra (Fig. 6.ii.1) show a maximum peak at 420 nm and a zero cross at 390 nm. The second derivative spectra (Fig. 6.ii.3) shows a peak at 392 nm and a zero cross at 379.8 nm. Therefore 420 nm and 392 nm respectively were selected for the first and second order derivative spectrophotometric determination of Mo (VI). The peak height was plotted against the amount of Mo (VI) to obtain the calibration curve.

First derivative method

The first derivative spectra of the Mo (VI) – 2-AAINH complex at different concentrations of Mo (VI) recorded and are presented in Fig. 6.ii.1. To determine the amount of Mo (VI) present, a plot was made between the amount of Mo (VI) and the derivative amplitude at 420 nm and showed in Fig. 6.ii.2. The plot was linear and obeyed the equation $A = 0.0449C + 0.0001$. The first derivative method allowed the determination of Mo (VI) in the range of 0.24 - 7.67 $\mu\text{g mL}^{-1}$. The standard deviation of the method for ten determinations of 2.396 $\mu\text{g mL}^{-1}$ of Mo (VI) was ± 0.0090 .

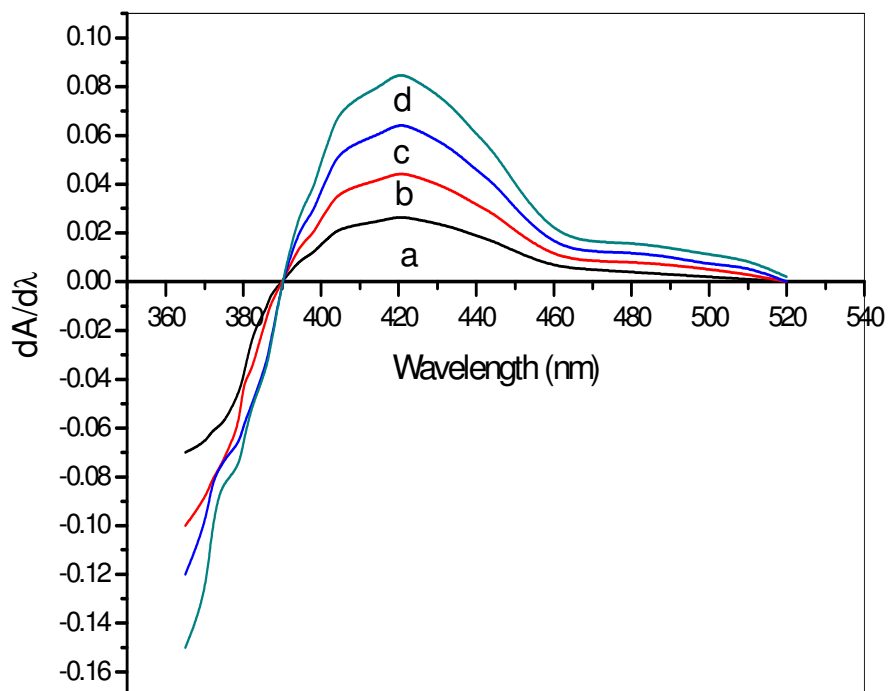


Fig. 6.ii.1. First derivative spectra of Mo(VI) – 2-AAINH Vs reagent blank
 Mo(VI) ($\mu\text{g mL}^{-1}$) = (a) 0.4797; (b) 0.9594; (c) 1.4391; (d) 1.9188

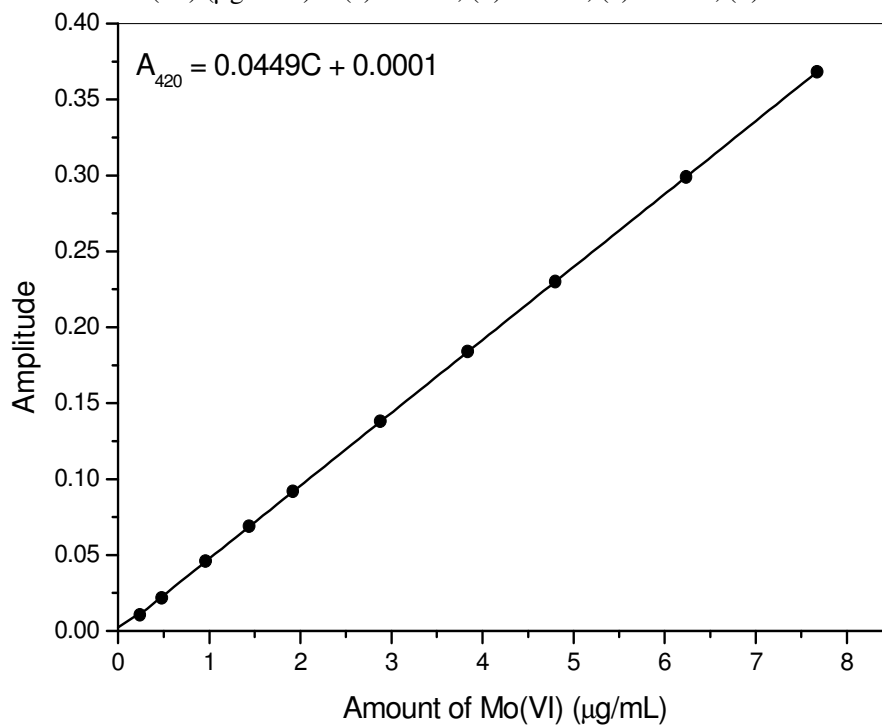


Fig. 6.ii.2. Beer's law plot of first derivative data
 $[2\text{-AAINH}] = 1 \times 10^{-3} \text{ M}$
 $\text{pH} = 3.0$

Second derivative method

The second derivative spectra (Fig. 6.ii.3) show maximum amplitude at 392nm. The derivative amplitudes at 392 nm were proportional to the concentration of Mo (VI). A plot was made between the amount of molybdenum (VI) and derivative amplitude and shown in Fig. 6.ii.4. The plot was linear in the range of 0.12-7.67 $\mu\text{g mL}^{-1}$ of Mo (VI). The standard deviation of the method for ten determinations of 0.479 $\mu\text{g mL}^{-1}$ of Mo (VI) was ± 0.0033 .

Effect of foreign ions

The effect of various cations and anions on the derivative amplitude was studied by following the general procedure 3k. It was noticed that all the ions that did not interfere in the zero order determinations of Mo (VI) (cf. Table 6.i.3) also did not interfere in the first and second derivative spectrophotometric determinations. Cu (II) tolerable in 5-fold excess in zero order method, is tolerable up to 20-fold excess in second order derivative spectrophotometric method. The metal ions Ru (III) and Pt(IV) interferes in five fold excess in zero order method and is tolerable upto 50-fold excess in second derivative method.

Application

Among the 1st and 2nd derivative methods, 2nd derivative method was more sensitive. Hence, this method was applied to determine the amount of molybdenum in alloy steels. The steel samples were brought into solution by the procedure 3(l).

Procedure

To a 10ml volumetric flask containing 5ml of buffer (pH 3.0) solution, 1ml of 2-AAINH ($1 \times 10^{-2}\text{M}$) solution, 1330 μg of Citrate (to mask Cu) and an aliquot of the sample solution were added and made up to the mark with distilled water. The second derivative spectrum was recorded and the derivative amplitude at 392nm was measured from which the amount of Mo (VI) present in the sample was determined from a pre-determined calibration plot. The results are presented in Table 6.ii.1.

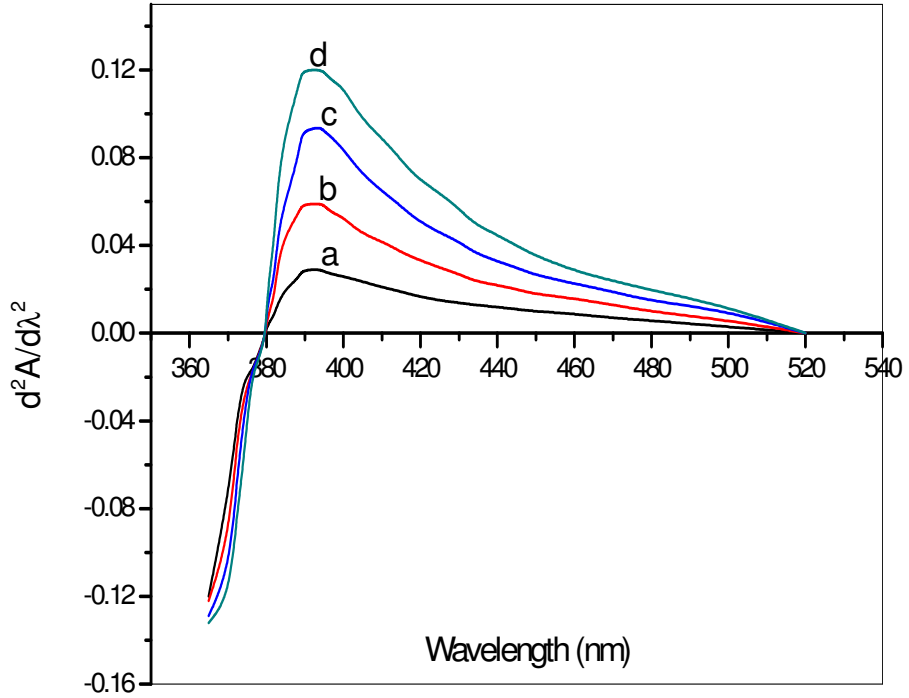


Fig. 6.ii.3. Second derivative spectra of Mo(VI) – 2-AAINH Vs reagent blank
 Mo(VI) ($\mu\text{g mL}^{-1}$) = (a) 0.4797; (b) 0.9594; (c) 1.4391; (d) 1.9188

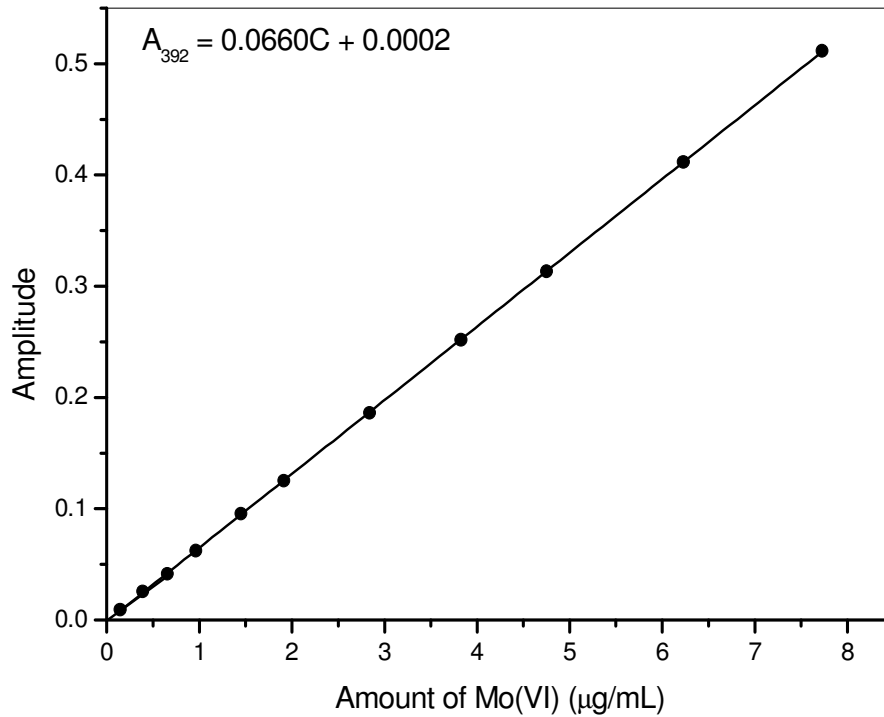


Fig. 6.ii.4. Beer's law plot of second derivative data
 [2-AAINH] = 1×10^{-3} M
 pH = 3.0

Table 6.ii.1
Analysis of Molybdenum in various alloy and steel samples

| Sample | Amount of Mo (%) | | Relative error (%) |
|------------------------|------------------|--------------|--------------------|
| | Certified value | Found value* | |
| NBS 362 ^a | 0.068 | 0.071 | +4.41 |
| JSS 169-3 ^b | 0.064 | 0.062 | -3.125 |
| JSS 171-3 ^c | 0.035 | 0.037 | +5.71 |

* Average of five determinations.

a = 0.068 Mo; 0.16 C; 1.04 Mn; 0.39 Si; 0.04 V; 0.084 Ti ; 0.20 W; 0.016 Sn; 0.09

Al; 0.19 Zr; 0.013 Sb; 0.50 Cu; 0.59 Cr; 0.30 Co; 0.09 As.

b = 0.064 Mo; 0.013 Ti; 0.005 As; 0.050 Ni; 0.011 Sn; 0.095; 0.045 Al; 0.0006 Ca.

c = 0.035 Mo; 0.036 Ti; 0.045 As; 0.11 Ni; 0.034 Sn; 0.067 Cr; 0.040 Al; 0.0013 Ca.

Comparison of the results

The results obtained in zero order and derivative spectrophotometric methods for Mo (VI)- 2-AAINH complex were compared and presented in Table 6.ii.2. From this it was noticed that in derivative spectra, the peak position shift towards higher wavelengths and Beer's law range was also improved compared to zero order method.

Table 6.ii.2
Comparison of the results for Mo (VI)

| Parameter | Zero order | First derivative | Second derivative |
|---|------------------------|------------------|-------------------|
| Analytical wave length (nm) | 385 | 420 | 392 |
| Molar absorptivity (L mol ⁻¹ .cm ⁻¹) | 1.21 × 10 ⁴ | – | – |
| Beer's law range (µg mL ⁻¹) | 0.49 – 7.34 | 0.24 - 7.67 | 0.12 - 7.67 |
| Angular coefficient (m) | 0.1215 | 0.0479 | 0.0660 |
| Y-intercept (b) | 0.0308 | 0.0001 | 0.0002 |
| Correlation coefficient (r) | 0.9994 | 0.9997 | 0.9998 |
| Standard derivation (s) | ±0.0012 | ±0.0090 | ±0.0033 |

Discussion

The present direct spectrophotometric method is simple, fast, and sensitive for the determination of Mo(VI). The metal ion reacts with 2-amino acetophenone isonicotinoyl hydrazone forming yellow coloured water soluble complex in acidic pH condition. The yellow colour was stable for more than 48 hours. The absorption spectrum of [Mo(VI) - 2-AAINH] complex showed maximum absorbance at 385 nm, the reagent absorbance was negligible at this wavelength. A 15 fold molar excess of reagent was necessary to obtain maximum colour intensity with a given amount of metal ion.

The complex system was found to obey Beer's law in the range 0.49–7.34 $\mu\text{g mL}^{-1}$ with Molar absorptivity $1.21 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$, Sandell's Sensitivity $8.0 \times 10^{-3} \mu\text{g cm}^{-2}$. The present method was applied for the determination of molybdenum(VI) in food stuffs and in some alloy steels.

The stoichiometric studies on the yellow coloured water soluble complex showed a 1:1 composition. The stability constant of the complex was calculated as 4.5×10^6 . The analytical results obtained by the proposed method are in good agreement with the amounts of Mo(VI) added. In order to improve the sensitivity and selectivity of the analytical method proposed, an attempt has been made to develop derivative spectrophotometric methods for the determination of molybdenum(VI), in which Beer's law range is improved and tolerance limits of interference ions such as Cu (II), Ru (III) and Pt (IV) which were low in the direct method were improved in derivative method. The derivative method was applied for the determination of molybdenum(VI) in alloy steels. The results of the present method were compared with those of some of the reported spectrophotometric methods and are presented in Table 6.ii.3.

The results reveal that the present method is non-extractive, comparable in its sensitivity and selectivity with some of the reported methods establishing its place among the spectrophotometric methods for the determination of molybdenum.

Table 6.ii.3
Comparison of Analytical results of proposed method with already reported methods for Molybdenum

| Reagent used | λ_{\max} (nm) | pH | $\epsilon \times 10^4$ (l mol ⁻¹ cm ⁻¹) | Beer's law range ($\mu\text{g mL}^{-1}$) | Remarks | Ref. No |
|--|--------------------------|-----|---|--|---|-------------------|
| Alizarin red S in presence of a | 500 | - | 2.1 | 0.05-5.5 | Cu(II), Al(III) and Fe(III) seriously | 16 |
| 2,2'-Biquinoxalyl | 685 | - | 3.3 | 0.2-2.0 | Fe(III) and Cr(III) interfered seriously | 19 |
| Phenylfluorone and lauryl dimethylbenzylammoniumbromide | 526 | - | 10.5 | 0.02-0.14 | Low selectivity | 26 |
| Catechol violet in the presence of gelatin | 670 | - | 3.0 | 1.84-3.36 | Commonly associated metal ions and anions interfered | 27 |
| N-Phenylbenzohydroxamic acid | 395 | - | 0.32 | 0.9-45 | Low molar absorptivity | 28 |
| Salicylaldehyde Acetoacetic Acid Hydrazone | 470 | 1.0 | 1.6 | 0.097- 0.968 | The proposed method is applied for determination of trace Mo(VI) in alloy samples | 37 |
| 4-Hydroxybenzaldehyde thiosemicarbazone | 365 | 6.0 | 1.25 | 0.03837- 0.3837 | The proposed method is applied for determination of trace Mo(VI) in alloy samples | 38 |
| 2-Hydroxy-3-methoxy benzaldehyde thiosemicarbazone (HMBATSC). | 375 | 1.5 | 2.47 | 0.24-4.32 | The proposed method is applied for determination of trace Mo(VI) in alloy samples and food stuffs | 40 |
| 2-Amino Acetophenone Isonicotinoyl Hydrazone | 385 | 3.0 | 1.21 | 0.49-7.34 | - | Present method |

REFERENCES

1. Hughes, M.N., **The Inorganic chemistry of Biological process**, second edition, (John Wiley & sons, chichester, New York), P. 173 (1990).
2. Marczenko Z. and Lobinski, R., *Pure appl. Chem.*, **63**, 1627 (1991).
3. Cruthamel, C.E. and Johnson, C.E., *Anal. Chem.*, **26**, 1284 (1954).
4. Allen, S.H. and Hamilton, M.B., *Anal. Chim. Acta*, **7**, 483 (1952).
5. Reddy, B.K., Jaya Kumar, C., Sarma, L.S. and Reddy, R.V., *Chem. Anal. (Warsaw)*, **42**, 56 (1977); Ozkhan, E. and Atalay, T., *Turk. J. Chem.*, **19**, 60, (1995); Patil, S.S. and Swant, A.D., *Indian J. Chem. Technol.*, **8**, 88, (2001).
6. Chikhalikar, S. and Patel, K.S., *Chem. Anal. (warsaw)*, **43**, 209 (1998); Kamburova, M., Alexandrov, A. and Trifonov, K., *Chem. Anal.*, **35**, 637 (1994); Sergio, L.C.F., de Jesus, D. and Jane, S., *J. Brag. Chem. Soc.*, **7**, 109 (1996); Panwar, O.S. and Arova, S.K., *J. Indian Chem. Soc.*, **72**, 745 (1995); Reddy, V.K., Reddy, S.M., Reddy, P.R. and Reddy, T.S., *Indian J. Chem., Sect. A*, **39**, 557 (2000).
7. Di, J., Klu, Y., Tu, Y. and Bi, S., *Anal. Sci.*, **18**, 125 (2002).
8. Melwanki, M.B., Seetharamappa, J. and Masti, S.P., *Anal. Sci.*, **17**, 1121 (2001).
9. Alkan, M., Kharun, M. and Chmilenco, F., *Talanta*, **59**, 605 (2003).
10. Martinez-Vidal, J.L., Alba-Fernandez, A.A. and salinas, *Analyst* (London), **115**, 329 (1990).
11. Altanassova, D., *Indian J. Technol.*, **28**, 211 (1990).
12. Zeng, Shengnion, Zhang, Huashan; Xie, Shannei and Wuhan Daxue Xendo, *Ziran Kexueban*, **1**, 92 (Ch) (1990).
13. Tarek, M., *et al.*, *Anal. Sci.*, **6**, 61 (1990).
14. Li, Zanjun; Tang, Jan; Pan, Jiaomai, *Analyst* (Cambridge, United Kingdom), **126**(7) (2001).

15. Chandrasekhar L.P. and Mishra, R.K., *J. Indian Chem. Soc.*, **LXIII**, 920 (1986).
16. Dass R. and Mehta, J.R., *J. Indian Chem. Soc.*, **74**, 512 (1997).
17. Filik, H., Tutem E. and Apak, R., *Anal. Chim. Acta*, **505**, 77 (2004).
18. Hoshi, S., Konuma, K., Sugawara, K., Uto M. and Akatsuka, K., *Talanta*, **44**, 1473 (1997).
19. Baranowska, I., and Barszczewska, K., *Talanta*, **39**, 1205 (1992).
20. Tarek, M., Zaki, M., Abdel-Kader A.K. and Abdella, M.M., *Talanta*, **37**, 1091 (1990).
21. Sato, S., Iwamoto M. and Uchikawa, S., *Talanta*, **34**, 419 (1987).
22. Thimmaiah K.N., Lloyd W.D. and Chandrappa, G.T., *Microchem. J.* **32**, 281 (1985).
23. Bermejo-Barera, P., Vazquez-Gonzalez, J., Pazos-Naveira M.C. and Bermejo-Martinez, F., *Analyst*, **112**, 477 (1987).
24. Dass R. and Mehta, J.R., *Mikrochim. Acta*, **113**, 37 (1994).
25. Dass R. and Mehta J.R., *Bull. Chem. Soc. Jpn.*, **67**, 999 (1994).
26. Kania K. and Buhl, F., *Chem. Anal. (Warsaw)*, **38**, 613 (1993).
27. Dimitrova, A., Atanasova, B. and Shishkov, A., *Nauchini Tr. Ploviduski Univ.*, **20**, 189 (1983); Chem. Abstr., **100**, 15024g (1984).
28. Agarwal Y.K. and Paghavan, T.N.V., *Indian J. Technol.*, **20**, 498 (1982).
29. Peshkova, V.M., Ivanova E.K. and Memon, S.D., *Anal. Khim.*, **35**, 486 (1980); Chem. Abstr., 93, 60428g (1980).
30. Lahiri S. and Ghosh, M., *Indian J. Chem.*, **30A**, 989 (1991).
31. Junwei Di, and Yifeng Tu, *Talanta*, **55**, 783 – 787 (2001).
32. Junwei Di, and Tianyu Yang, *Talanta*, **61**, 165 – 171 (2003).
33. Malik, A.K., Kaul, K.N., Lark, B.S., Faubel, W. and Rao, A.L.J., *Turk J. Chem.*, **25**, 99-105 (2001).
34. Dimitrov, Atanas, N., Lekovg, Vania, D., Gavazov, Kiril, B., Boyanov, Boyan, S., *Central European Journal of Chemistry*, **3**, 747 – 755 (2005).
35. Li Zaijun, A., Yang, Yulingb, Tang Jiana and Pan Jiaomaic, *Journal of Food Composition and analysis*, **18**, 561 – 569, (2005).
36. Derya Kara and Cennet Karadas, *Spectrochimica Acta Part-A*, Molecular and biomolucilar spectroscopy, 147(8), 158-162,(2015).

37. V.Srilalitha, A.Raghvendra Guruprasad, K.Ramanakumar,V.Sesagiri and L.K.R. **Che.,Bull. "POLITHNICA"Univ.(Timisoara),**55(69),2,107-110,(2010).
38. K.P.Satheesh, S.Ravichandran, VSN, N. Devanna, KBR, **International Journal of Chem Tech Research,** 3,4. 1740-1746,Oct-Dec-2011.
39. C.H.Kethani Devi, D.Gopala Krishna, N.Devanna, KBC, **RJPBCS** 1,3.808-825,July-Sep.2010.
40. A.P.R.,PRR, & VKR, **J.Chil.Chem.Soc.** 52,N4,1309-1313,2007.
41. Rameshwar Dass', Jithender Kumar Kapoor, Sunitha Gambhir., **Turkish Journal of Chemistry,**38.,328-337,2014.
42. Bhardwaj Punita S. **Journal of Environmental Research & Development,** 7, 4A, 1606-1609, April-June,2013..
43. Clark, L.J. and Axley, J.H., **Anal. Chem.,** 27(12), 2000–2003 (1955).