Benghazi University
Faculty of Science
Chemistry Department

"Optimization of the Critical Instrumental parameters in Analysis of some Trace Elements in Different Matrices by Flame Spectrometry"

A thesis submitted as partial fulfillment for the requirement of the degree of Master of Science in Chemistry

By

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BENGHAZI – LIBYA

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”قَالُوا سُبْحَانَكَ لَا عِلْمَ لَنَا إِلَّا مَا

عَلَّمْتَنَا إِنَّكَ أَنْتَ الْعَلِيمُ الْحَكِيمُ„

صَدَقَ اللَّهُ الْعَظِيمُ

Dedication To

My Be Loved Parent

And To My Wife

For All Love, Support,

And Help Through All

The Difficult Of My Study.

ACKNOWLEDGEMENT

In the name of Allah, most Gracious, most Merciful. A word of thanks giving to God, the source of all knowledge, by whose abundant grace this work has come to fruition.

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Finally to my parents, my brothers my sister, and my wife I extend my heartfelt gratitude for their continual prayers for me.

Atiea S. Samor

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Abbreviations and Acronyms

The following Abbreviations and Acronyms are used in this thesis

AAS	Atomic Absorption Spectrometry
FAAS	Flame Atomic Absorption Spectrometry
RSD	Relative Standard Deviation
HCL	Hollow Cathode Lamp
EDL	Electrodeless Discharge Lamp
PMT	Photomultiplier Tube
S/N	Signal-to-Noise ratio
BC	Background Correction
D lamp	Deuterium lamp
PVC	Polyvinyl Chloride
PFA	Prefluoroalkoxy Plastics
PE	Polyethylene

Abstract

The critical instrumental parameters are of significant effect during analyses of trace element by flame AAS.

Burner height and fuel-oxidant stoichiometry investigated for Chromium, Nickel, Manganese and Cadmium determination in standard solution and in highly interfering matrices (5% sodium chloride, serum and urine).

Addition of some releasing agents and additives to the samples during analysis were tested in order to reduce the background signal and enhance the sensitivity and reproducibility of the measurements.

CHAPTER (1)

INTRODUCTION

1.1 Atomic Absorption Spectrometry:

Atomic absorption spectroscopy is the term used when the radiation absorbed by atoms is measured. The application of AAS to analytical problems was considerably delayed because of the apparent need for very high resolution to make quantitative measurements. [1]

The spectra of atomic absorption of an element are made up of a series of resonance lines from the ground state to different excited states. The transition between the ground state and the first excited state is known as the first resonance line, being that of greatest absorption, and is the one used for analysis. The wavelength of the first resonance line of all metals and some metalloids is greater than 200 nm, while for most non-metals it is lower than 185 nm. The analysis for these cases requires modifications of the optical systems which increases the cost of atomic absorption instruments.[2]

1.1.1 Flame Atomic Absorption Spectrometry:

The flame technique is the oldest of the AAS techniques. For many years it was the ‘workhorse’ for the determination of secondary and trace elements and also for main constituents, and even nowadays it is difficult to imagine a routine analytical laboratory without this technique. Due to its simplicity and economy.[3]

The technique in flame atomic absorption is based on measuring absorption of resonance spectral line radiation by ground-state free atoms of the element, then the concentrations could be determined in (µg/ml).

Sensitivity in FAAS is indirectly expressed as *characteristic mass* (i.e. such concentration µg/ml of the element that gives the absorbance of 0.0044).

Repeatability of analysis in FAAS could be controlled by monitoring the relative standard deviation (RSD), in most cases RSD should be in range of (1 - 5 %).[4]

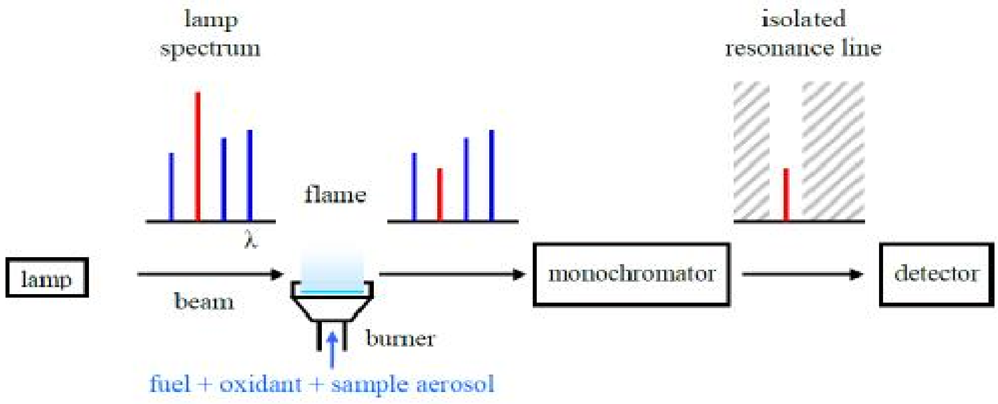

Figure (1.1): Schematic construction of a simple flame atomic absorption .[1]

In atomic absorption spectrometry, no ordinary monochromator can give such a narrow band of radiation as the width of the peak of the line of atomic absorption. In these conditions the Beer Law is not obeyed and the sensitivity of the method is reduced. Walsh demonstrated that a hollow-cathode, made of the same material as the analyte, emits narrower lines than the corresponding lines of atomic absorption of the atoms of the analyte in flame, this being the base of the instruments of atomic absorption.[5]

The main disadvantage is the need for a different lamp source for each element to be analyzed. The most frequently radiation energy source used in atomic absorption spectroscopy is the hollow cathode lamp.[2]

1.2 Parts of Flame Atomic Absorption Spectrometer:

There are five basic components of an atomic absorption instrument: The radiation source that emits the spectrum of the element of interest, an "absorption cell" in which atoms of the sample are produced (flame), a monochromator for light dispersion, a detector, which measures the light intensity and amplifies the signal, and display that shows the reading after it has been processed by the instrument electronics, and there are two basic types of atomic absorption instruments: single- beam and double-beam.[5]

1.2.1 Radiation source:

In AAS the radiation source is a device to generate electromagnetic radiation with given properties; the radiation can be generated for example in a low pressure electrical discharge or in low pressure plasma. Sources in sealed containers with stationary fill gases are termed lamps or spectral lamps. In AAS, line sources are preferred which emit the spectral lines of one or more elements. Hollow Cathode Lamps (HCLs) and Electrodeless Discharge Lamps (EDLs) are the main types of lamp employed. Next to line sources, continuum sources also find application as primary radiation sources in AAS under given prerequisites. However, they are used much more frequently for background correction.[6]

1.2.1.1 Hollow-Cathode Lamp:

As the name suggests, the central feature is a hollow cylindrical cathode, lined with the metal of interest. The lamp is contained within a glass envelope filled with an inert gas (usually Ne or Ar) at 1-5 Torr.[7]

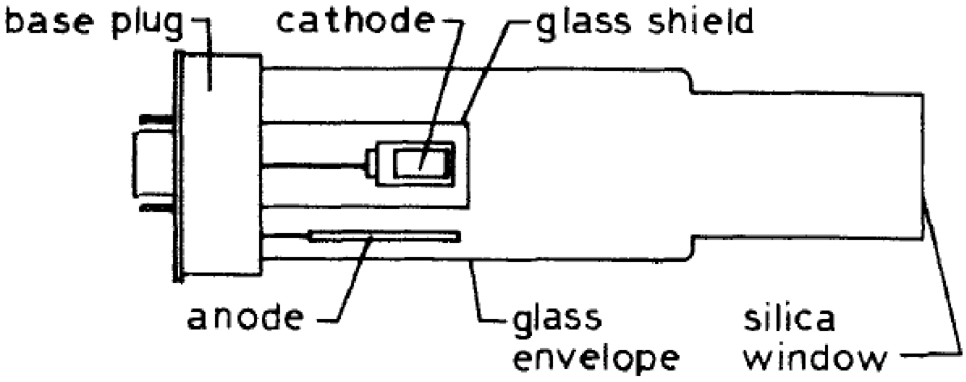

Figure (1.2): Cross section through a hollow-cathode lamp.[8]

A potential of about 500 V is applied between the electrodes and, at the pressures used, the discharge concentrates into the hollow cathode. Typically, currents of 2-30 mA are used. The filler gas becomes charged at the anode, and the ions produced are attracted to the cathode and accelerated by the field. The bombardment of these ions on the inner surface of the cathode causes metal atoms to sputter out of the cathode cup. Further collisions excite these metal atoms, and a simple, intense characteristic spectrum of the metal is produced.[9]

1.2.1.2 Deuterium lamp:

A spectral lamp with deuterium as the discharge gas in a quartz bulb, for some applications hydrogen has also been used as the discharge gas. The deuterium lamp emits a sufficiently high radiant power in the short wavelength range from about 190 nm to 330 nm, the deuterium lamp is continuum source, is used for sequential or quasi-simultaneous background measurement and correction.[10]

1.2.2 Atomizer:

The atomizer is the sample cell of the AAS system. The atomizer must produce the ground state free gas phase atoms necessary for the AAS process to occur. The analyte atoms are generally present in the sample as salts, molecular compounds, and/or complexes. The atomizer must convert these species to the reduced, free gas phase atomic state. The atomizer generally does this via thermal energy and some chemistry. To create a flame, we need to mix an oxidant gas and a fuel gas, and light the mixture. In modern commercial flame AAS; two types of flames are used. The first is the air– acetylene flame, where air is the oxidant and acetylene is the fuel. The second type of flame is the nitrous oxide–acetylene flame, where nitrous oxide is the oxidant and acetylene is again the fuel. The fuel and oxidant gases are mixed in a burner system, called a Premix burner.[11]

An exploded view of one type of commercial flame atomic absorption burner is shown in Figure 1.3(a). In this design, the fuel gas is introduced into the mixing chamber through one inlet while the oxidant gas is introduced through the sidearm on the nebulizer. The premix burner design generates laminar gas flow and this result in a very steady flame. The steady flame generates less noise due to "flame flicker"; this improves precision. Mixing the gases in the mixing chamber eliminates the safety hazard of having a combustible gas mixture piped through the laboratory.

The flame burns just above the burner head, along the slot shown in the figure. The sample is introduced into the burner in the form of a solution. The solution is aspirated into the nebulizer, which is basically a capillary tube. The nebulizer sprays the solution into the mixing chamber in the form of a fine aerosol. Three nebulizer designs are shown schematically in Figure 1.3(b).

The term "to nebulize" means to convert to a fine mist, like a cloud. The solution exits the capillary tube at high velocity and breaks into tiny droplets as a result of the pressure drop created.

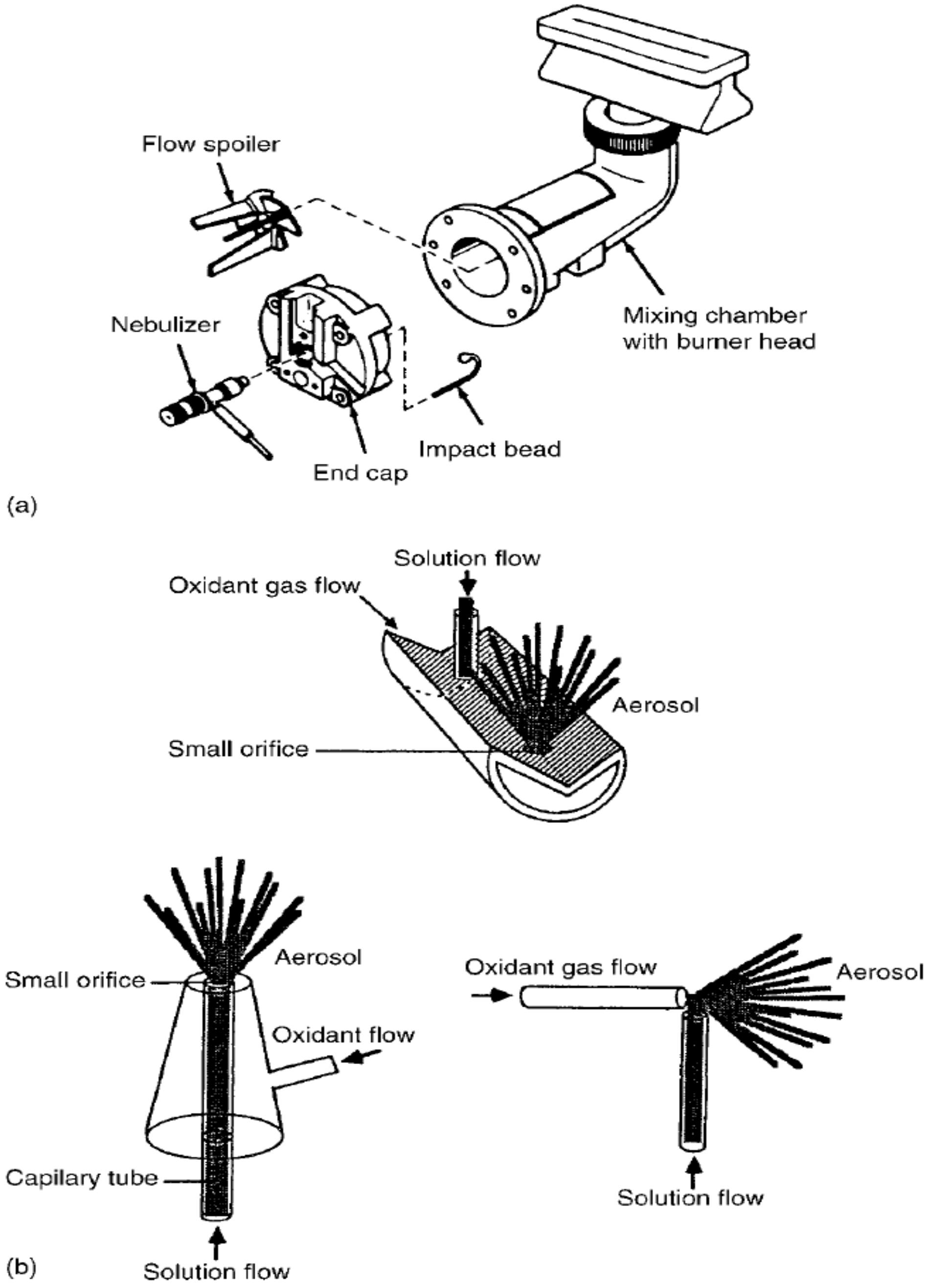

Figure (1.3): (a) Premix burner system. (b) Schematic nebulizer designs. (Top): modified Babington type; (left) concentric (the most common in FAAS); (right) cross-flow type.[12]

Kinetic energy transfer from the nebulizer gas overcomes the surface tension and cohesive forces holding the liquid together. The fuel and oxidant gases carry the sample aerosol to the base of the flame. In the flame the sample aerosol is desolvated, vaporized, and atomized to form free gas phase atoms of the analyte.

When the sample solution passes through the nebulizer, an aerosol is formed, but the droplets are of different sizes. As a droplet enters the flame, the solvent (water or organic solvent) must be vaporized, the residue must vaporize, and the sample molecules must dissociate into atoms. The larger the droplet, the more inefficient this process is. The two devices shown in Figure 1.3(a) are used to overcome this problem.[12]

The impact bead is made of glass, quartz, or ceramic, and is placed directly in front of the nebulizer spray inside the mixing chamber. The impact bead improves nebulization efficiency by breaking larger droplets into smaller ones through collision of the spray with the bead. The flow spoiler is a piece of polymer or other corrosion-resistant material machined into three or more vanes.

The flow spoiler is placed in the mixing chamber, about midway between the end cap and the burner. It physically removes larger droplets from the aerosol through collision while smaller droplets pass through the openings between the vanes. The larger droplets drain from the mixing chamber through a drain opening. The aim of this system is to produce an aerosol with droplets 4 mm in diameter. The two devices may be used alone or in combination.[13]

The drain opening is connected to a liquid waste container with a length of polymer tubing. It is extremely important that there be a trap between the drain opening and the waste container to prevent the free flow of flame gases out of the burner assembly.

The nebulizer capillary is usually made of stainless steel but other materials such as Pt, Ta, and polymers may be used for corrosive solvents when contamination from the elements in steel must be avoided. The burner head is constructed either of stainless steel or titanium.

Different sizes and geometries of burner heads are used for various flames. A 5 cm long single slot burner head with a narrower slot is used for nitrous oxide–acetylene flames. The flame is supposed to propagate up from the burner head. It will do so if the linear gas flow rate through the burner slot is higher than the burning velocity of the flame. Burning velocity is a characteristic of the flame type; both nitrous oxide–acetylene and air–acetylene flames have low burning velocities. If the premixed gas flow rate is less than the burning velocity.[14]

The air-acetylene flame is the most widely used flame. It is stable, simple to operate and produces sufficient atomization to enable good sensitivity and freedom from interferences for many elements. It is not only necessary for the flame to atomize the analyte, but also to break down any refractory compounds which may react with or physically entrap the analyte. Atomization, as we shall see, occurs both because of the high enthalpy and temperature of the flame, and through chemical effects. Thus, increasing the oxygen content of the flame above the approximately 20% normally present in air, while raising the flame temperature, does not necessarily enhance atomization, because more refractory oxides may be produced.

Making the flame more fuel rich lowers the temperature but, by making the flame more reducing, increases the atomization of the elements such as molybdenum and aluminium, the type of oxidant and fuel, along with the burning velocity, affect the temperatures in the various zones of flame, and this in turn will determine the number of atoms formed during dissociation. [15]

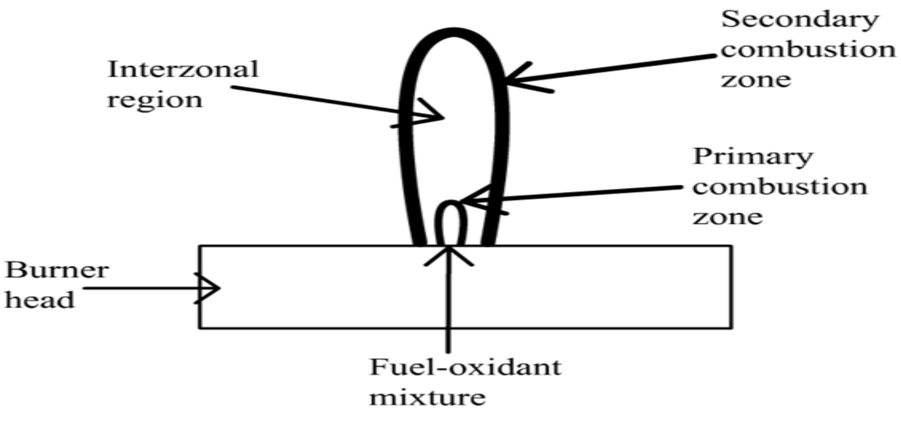

Figure (1.4): various zones of flame.[15]

The temperature will determine the optimum region for maximum atomization and will vary from one element to another, and varies with the height above the burner head as well as type of flame .[16]

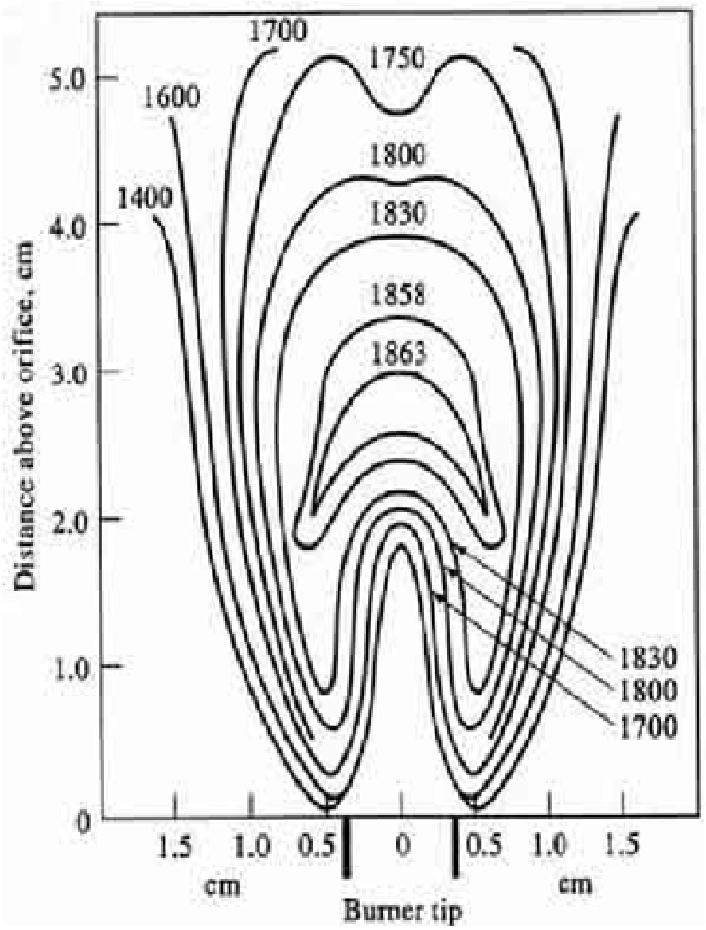

Figure (1.5): Flame profile of air-acetylene flame.[16]

1.2.3 Monochromator:

A monochromator is required to separate the absorption line of interest from other spectral lines emitted from the HCL and from other elements in the atomizer that are also emitting their spectra. Because the radiation source produces such narrow lines, spectral interference is not common. Therefore the monochromator does not need high resolution.[17]

A typical monochromator is shown in Figure (1.6); the most common dispersion element used in AAS is a diffraction grating. The grating disperses different wavelengths of light at different angles. The grating can be rotated to select the wavelength that will pass through the exit slit to the detector.

All other wavelengths are blocked from reaching the detector. The angle of dispersion at the grating is a function of the density of lines ruled on the grating. The more lines/mm on the grating, the higher is the dispersion.

Higher dispersion means greater separation between adjacent lines. A high dispersion grating permits the use of wider entrance and exit slits on the monochromator to achieve the same resolution. Wider slits allow more light to pass through the system to the detector. Large high-quality gratings with high dispersion are expensive, but they offer better energy throughput than cheaper low-dispersion gratings.[18]

In addition to the number of lines ruled on the grating, the blaze angle affects the intensity of diffracted wavelengths.[19]

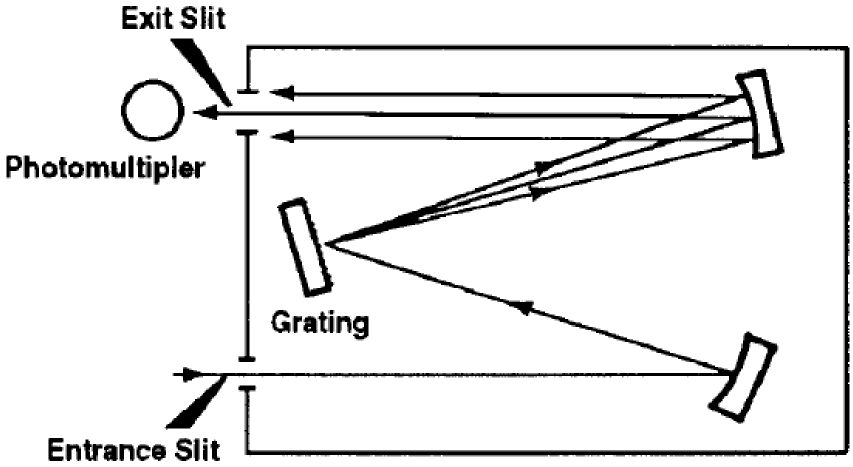

Figure (1.6): typical grating monochromator layout.[19]

1.2.4 Detector:

Is operating on the photoelectric principle are used exclusively for the detection of radiation in AAS. The requirements of AAS are best met by broad band photomultipliers (multialkali types).[20]

The photomultiplier tube (PMT) is a radiation detector in which the incident radiation falling on a photocathode causes the emission of primary electrons (outer photoelectric effect) which are released into the surrounding vacuum. Resulting from the applied dynode voltage each primary electron is accelerated so rapidly that when it strikes a dynode two to ten secondary electrons are emitted, leading to a cascade effect as shown schematically in Figure (1.7).

Nevertheless there are limits to the voltage that can be applied, since this leads to a higher dark current and thus to increased noise. In extreme cases the dynodes can become saturated.[21,22]

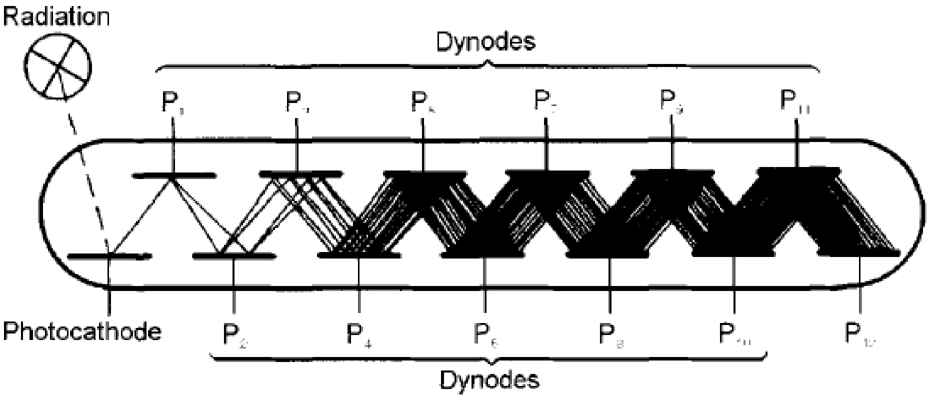

Figure (1.7): Schematic of a photomultiplier with 11 dynodes.[23]

PMTs with 9 to 12 dynodes are mostly used in AAS so that the anode output varies as the sixth to tenth power of changes in the applied voltage. Since the output signal is so extremely sensitive to changes in the applied voltage, the stability and freedom from noise of this source are especially important.[24]

1.3 Signal and Noise (sensitivity):

All instruments measure some chemical or physical characteristic of the sample; with flame AAS one can measure how much light is absorbed by the sample at a given wavelength.[25]

A detector of some type makes the measurement and then the detector response is converted to an electrical signal. The electrical signal should be directly related to the chemical or physical property being measured and that should be related to the amount of analyte present.[26]

Ideally, the signal would represent only information related to the analyte. When no analyte is present, there should be no signal, In Figure (1.8) show some signals from a spectrometer that is measuring the amount of light emitted by a sample at a given wavelength. The three traces in Figure (1.8) show a peak, which is the signal at the emission wavelength. The response on either side of the peak is called the baseline.[27]

An ideal signal for intensity of light emitted by the analyte vs. wavelength would be a smooth baseline when no light is emitted and a smooth peak at the emission wavelength, as shown in Figure (1.8- a). In this case, when the instrument does not detect the analyte, there is no signal, represented by the flat base line.

When the instrument detects the analyte, the signal increases; when the instrument no longer detects the analyte, the signal decreases back to the baseline.

In this case the entire signal (the peak) is attributed to the analyte. In practice, however, the recorded signal and baseline are seldom smooth, but include random signals called noise. [28]

All measured signals contain the desired information about the analyte and undesirable information, including noise. Noise can originate from small fluctuations of various types in the instrumentation, in the power provided to the instrument, from external sources such as TV and radio stations, other instruments nearby, building vibrations, electrical motors and similar sources, and even from fundamental quantum effects that cannot be eliminated. Provided that the signal is sufficiently greater than the noise, it is not difficult to make a reliable measurement of the desired analyte signal. The signal-to-noise ratio, S/N, is a useful quantity for comparing analytical methods or instruments.

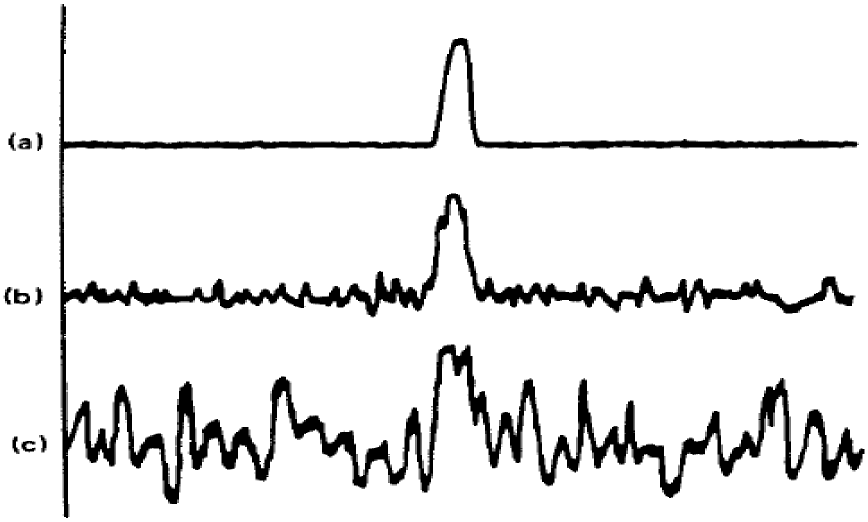

Figure (1.8): Signal vs. wavelength with different noise levels: (a) no detectable noise, (b) moderate noise, and (c) high noise.[29]

In Figure (1.8- b) the noise level is increased over that in Figure (1.8- a) and is superimposed on the signal. The value of the signal is less certain as a result of the noise.

The measurement is less precise, but the signal is clearly discernible. In Figure (1.8- c) the noise level is as great as the signal, and it is virtually impossible to make a meaningful measurement of the latter.

It is very important to be able to separate data-containing signals from noise. When the signal is very weak, as it might be for trace amounts of analyte, the noise must be reduced or the signal enhanced. Noise is random in nature; it can be either positive or negative at any given point, as can be seen in Figure (1.8- b and c). Because noise is random, it can be treated statistically.[29]

1.4 Classification of Interferences in FAAS:

The presence of concomitants in the test sample can cause interferences in the determination of the analyte. The interference can influence both the attainable precision and the trueness. However, interference only leads to a measurement error if it is not eliminated, or if it is not taken into consideration in the evaluation process, by suitable measures.

Such measures can be instrumental, such as background correction, or the choice of a suitable calibration technique, such as the analyte addition technique, or the use of chemical additives. An influence on the analyte signal by the atomizer, for example by the flame gases or the graphite material, or by the solvent, is not considered as an interference since the effect is usually the same for test sample and calibration solutions.[30]

Interferences in spectrochemical analysis can be classified according to a number of aspects. The various categories are not mutually exclusive but rather complement each other in characterizing the interference. Frequently the distinction is made between specific and non-specific or between additive and multiplicative interferences. In the following we shall largely adhere to the IUPAC recommendations; these recommendations have been accepted into various national and international standards. Accordingly, interferences are divided generally into spectral and non-spectral interferences.[31]

Spectral interferences are due to the incomplete isolation of the radiation absorbed by the analyte from other radiation or radiation absorption detected and processed by the electrical measuring system. With non-spectral interferences the number of free analyte atoms, and thus the measurement signal, is affected directly.[32]

Non-spectral interferences are most conveniently classified according to the place or time of their occurrence.[29]

1.4.1 Eliminating Interferences:

1.4.1.1Spectral interferences:

Caused by direct line overlap are best avoided by changing to an alternate analytical line. A sufficiently large number of alternate lines are available; especially for the transition elements. In the case of background attenuation it is also possible to use an alternate analytical line to avoid or eliminate the interference.[33]

The interference frequently decreases markedly with increasing wavelength. Like non-spectral interferences, spectral interferences can be reduced, or on occasions even eliminated, by diluting the test sample solution. Nevertheless, there are limits to this technique since the analyte is also always diluted. If it is really possible to prepare a true matrix blank solution for any given test sample solution, the chance is given not only to recognize the interference but also to eliminate it.[34]

It is merely necessary to subtract the measurement value for the matrix blank solution, which can only derive from background attenuation, from that of the test sample solution. Since background attenuation is caused by non-volatilized or non-dissociated sample constituents, this interference can be reduced or even eliminated by raising the effective temperature in the atomizer. This can be achieved in

FAAS for example by changing from the air-acetylene to the nitrous oxide-acetylene flame.[35]

Nowadays instrumental techniques are used almost exclusively to eliminate interferences caused by background attenuation. Continuum source Background Correction usually suffices for the interferences that occur in FAAS, on the other hand, it is often insufficient, it mostly leads to a better signal to noise ratio (S/N) . [36]

1.4.1.2 Non-spectral interferences:

Direct influences on the sensitivity, can generally be eliminated by matching the test sample solutions and the calibration solutions as closely as possible. In the ideal case a calibration solution contains not only the same solvent and the same additives as the test sample solution, but also the same concomitants. A calibration solution should thus according to definition correspond to the test sample solution except for the concentration of the analyte.

If this were really the case we would not observe any interference since the matrix effects influence the analyte in the test sample and calibration solutions to the same extent. Albeit this ideal case can rarely be realized in practice. In the first place the exact composition of a test sample frequently is not known and in many cases cannot be reproduced. Even if these requirements are met, reagents of the highest purity and often considerable effort are required to prepare a calibration solution that corresponds exactly to the test sample solution. [37]

Since in many laboratories large numbers of samples with varying compositions must be analyzed, this procedure is in any case unrealistic. Match the calibration solution to the test sample solution. It often suffices to use the same solvent and to match a main constituent of the test sample. In the flame technique in particular routine determinations can frequently be performed against simple calibration solutions.[38]

The application of the analyte addition technique is recommended when the composition of the test samples changes frequently or complex matrix effects are present. Since an individual calibration curve is established for each test sample by adding calibration solutions, the ideal case described above is virtually attained. All non-spectral interferences should in effect be eliminated using this technique, except those that depend on the concentration of the analyte.[39]

Ionization interference is most definitely dependent on the concentration, so that the analyte addition technique cannot be applied to eliminate this interference. The interferences that can be observed under other conditions are usually eliminated, so that the application of the analyte addition technique is superfluous. Ideally the analyte addition technique can be applied to eliminate all non-specific interferences, such as transport interferences in FAAS.[40]

If this technique is used to eliminate specific interferences, then great care must be taken to ensure that the influences on the analyte are the same in both the test sample and the added solutions. The reference element technique, in which another element is added to the sample in known concentration, is, by definition, only suitable for the elimination of non-specific interferences, such as transport interferences. Since logically all specific interferences are specific to the given analyte, it cannot be expected that they can be eliminated by measuring another element.

As already explained this technique makes very high demands on the instrument and the analytical technique, and is thus little suited for AAS; the loss in sensitivity also leads to deterioration in the signal to noise ratio (S/N).[41]

A technique used widely for the elimination of interferences is the addition of spectrochemical buffers to the test sample and calibration solutions.[30]

Depending on the type of interference, different buffers with varying modes of action can be employed. Nebulization aids, for example, can be used to bring the physical properties of the solutions, such as viscosity or surface tension, into line and thereby eliminate transport interferences. Volatilizers are a further group of spectrochemical buffers that improve the volatilization or atomization of the analyte by converting it into a more suitable form.

Releasers are frequently used to prevent the analyte from entering thermally stable compounds. This technique for the elimination of solute-volatilization and vapor-phase interferences is based on the knowledge that these interferences occur during desolvation during initial precipitation from the saturated solution, or through rearrangement reactions in the solid particles. An ionization buffer is added to suppress ionization; an easily ionized element, such as cesium or potassium that increases the concentration of free electrons in the atomizer, thereby suppressing and stabilizing ionization of the analyte.[42]

1.4.2 **Background Correction**:

Absorption by the flame atomizer itself as well as by concomitants introduced into the flame can cause serious problems in atomic absorption. Rarely are there interferences from absorption of the analyte line by other atoms since the hollow-cathode lines are so narrow. Molecular species can absorb the radiation and cause errors in AA measurements, however .[43]

The total measured absorbance (A_T) in AA is the sum of the analyte absorbance (A_A) plus the background absorbance (A_B) :

$$A_T = A_A + A_B$$

Background correction schemes attempt to measure (A_B) in addition to (A_T) and to obtain the true analyte absorbance by subtraction:

$$(A_A = A_T - A_B)$$

Continuum Source Background Correction (Deuterium lamp) is popular background correction used in commercial (A_A) spectrometers.

A deuterium lamp and the analyte hollow cathode are directed through the atomizer at different times. The hollow-cathode lamp measures the total absorbance (A_T), while the deuterium lamp (D) provides an estimate of the background absorbance (A_B). The computer system or processing electronics calculates the difference and reports the background-corrected absorbance. This method has limitations for elements with lines in the visible range because the deuterium lamp intensity becomes quite low in this region.[44]

1.5 Heavy metal as sources of pollution of the environment:

Environmental pollution as a result of man's increasing activities such as burning of fossil fuels and automobile exhaust emission has increased considerably in the past century due mainly to significant increases in economic activities and industrialization. [45]

Burning of fossil fuels and petroleum industry activities have been identified as primary sources of atmospheric metallic burden leading to environmental pollution. Several studies have shown that heavy metals such as lead, cadmium, nickel, manganese and chromium amongst others are responsible for certain diseases. [45]

In general, heavy metals are systemic toxins with specific neurotoxic, nephrotoxic, fetotoxic and teratogenic effects. Heavy metals can directly influence behavior by impairing mental and neurological function, influencing neurotransmitter production and utilization, and altering numerous metabolic body processes. [45]

Systems in which toxic metal elements can induce impairment and dysfunction include the blood and cardiovascular, eliminative pathways (colon, liver, kidneys, skin), endocrine (hormonal), energy production pathways, enzymatic, gastrointestinal, immune, nervous (central and peripheral), reproductive and urinary that have lethal effects on man and animals.[45]

These diseases include abdominal pain, chronic bronchitis, kidney disease, pulmonary edema (accumulation of fluid in the lungs), cancer of the lung and nasal sinus ulcers, convulsions, liver damage and even death.[46]

1.5.1 Cadmium:

Cadmium makes up about 5 x10^{-5} % of the Earth's crust and is thus one of the rarer metals. In very low concentrations Cd is nowadays ubiquitous. The source of some occurrences, e.g. in sea-water, is unknown. The distribution of Cd on land is a consequence of emissions from industrial plants, especially zinc smelters and iron and steel works, and also from waste incineration plants and brown-coal-fired power stations. About a third of the Cd production is used in the manufacture of batteries. The use of Cd as an anticorrosive for iron and other metals is in second place. [47]

The use of Cd pigments and Cd soaps as stabilizers for PVC is also a major application. The accumulation of Cd in the liver and kidneys is critical. Significantly higher concentrations of Cd are found in smokers compared to nonsmokers. Since a carcinogenic potential is suspected, Cd and a number of its compounds are included in various national and international lists stipulating the maximum concentration at the workplace.

The stability of Cd solutions has been the subject of numerous investigations. Sorption losses take place at pH values > 4. These losses can be effectively suppressed by acidifying the solutions to pH 2 with nitric acid; acidification should be performed at sampling since adsorption losses are in part irreversible.[48]

Cadmium can be easily atomized and thus determined without any noteworthy interference in the air-acetylene flame. The characteristic concentration is 0.02 mg/L at the 228.8 nm resonance line. With continuum source BC a spectral interference can take place at this line in the presence of high iron concentrations due to overcorrection. The analytical line at 326.1 nm is suitable for determining higher Cd concentrations; the characteristic concentration is about 6 mg/L, so that excessive dilution can be avoided.[3]

1.5.2 Nickel:

The proportion of Ni in the Earth's crust is estimated to be 0.015 %; Ni is thus at position 22 in the abundance list of the elements. Since iron meteorites contain on average 8-9 % Ni, it is surmised that larger quantities of Ni are contained in the Earth's core. The greatest part of the production of Ni is used in the steel industry and for the production of alloys. Organ nickel compounds play an important role in a number of polymerization processes.

Physiologically Ni is one of the trace elements; the human body contains about 10 mg. little is known about the biological role that Ni plays, but it appears to participate in carbohydrate metabolism; the concentration in serum and urine is around 0.5 μg/L. Inhalable dusts or aerosols of Ni metal or compounds, such as are produced during production and processing, are classified as hazardous substances and are carcinogenic, nickel is thus an important element in the areas of toxicology and industrial hygiene.[49]

The stability of aqueous Ni solutions has been investigated under varying storage conditions and in a variety of container materials. Sorption losses were significant after 24 hours in borosilicate glass if the pH value of calibration solutions acidified with hydrochloric acid was > 5. Slightly acidified solutions containing *5* and *50* μg/L Ni could be stored in PFA bottles for up to *50* days without losses, investigated the stability of urine samples with respect to their Ni content.[50]

Nickel is among the elements determined frequently by AAS; the best characteristic concentration of 0.04 mg/L is obtained in the air-acetylene flame at the 232.0 nm resonance line. In order to use this line a spectral slit width of 0.2 nm is necessary the strong emission lines at 231.716 nm and 232.138 nm cause considerable curvature of the calibration curve and a reduction of the sensitivity. Since the 232.0 nm line exhibits a noticeably non-linear calibration curve, even with a slit width of 0.2 nm, it is not particularly suitable for determining higher Ni concentrations.

For this purpose the line at 341.5 nm with a characteristic concentration of 0.2 mg/L is more suitable. This line even allows the use of wider spectral slit widths of up to 0.7 nm and thus provides a good S/N ratio, slight spectral interferences can occur at a number of these lines, particularly with multielement lamps that contain cobalt, so that critical scrutiny of the lines and the signals is recommended.[51]

In an oxidizing (fuel-lean) air-acetylene flame the determination of Ni appears to be largely free of interferences found that high concentrations of Al, Co, Cr, Cu, Mn, Mo, V, and W did not cause interferences. Likewise, HCI, HNO, H_2SO_4 and H_3PO_4, had no influence. Nevertheless, careful optimization of the burner height and the flame stoichiometry are required. In a less oxidizing flame, interferences due to iron and chromium become noticeable.[52]

Related the various effects of other concomitant elements found with nonoptimum gas settings and observation height to the dissociation energies of the corresponding monoxides. The potential influences of iron and chromium can be eliminated by the use of the nitrous oxide-acetylene flame; the characteristic concentration in this flame at the 232.0 nm resonance line is only around 2 mg/L.[3]

1.5.3 Manganese:

Manganese is the second most abundant heavy metal; it is present to about 0.1 % in the Earth's crust and is in twelfth position in the abundance list of the elements. Far higher concentrations are present in the Earth's core. As a non-noble metal it is only present in nature in the form of its compounds in the + 2 through +7 oxidation states. It is to be found as a trace element in virtually all soils, and frequently together with iron in ground waters.[53]

Large quantities of Mn are to be found in nodules on the seabed. Manganese is an essential trace element that is present in all living cells. It is resorbed by plants in the form of Mn (II) salts and plays a major role in photosynthesis. It is also an essential trace element in animals and is present in numerous oxidoreductases and other enzymes. The human body contains about 20 mg Mn. A daily ingestion of at least 3 ng is considered as necessary.[54]

The stability of aqueous Mn solutions has been investigated in various container materials and under varying conditions of storage. Losses of Mn start at pH values > 2.5, increase with increasing pH value, and are virtually quantitative at a pH value of 8.

The losses on glass surfaces are significantly higher than on PE. In PFA bottles dilute, acidified solutions could be stored for over a year. Manganese can be determined in the air-acetylene flame without major interferences; the best characteristic concentration of 0.03 mg/L can be attained at the 279.5 nm analytical line.

Manganese is an exception in that several spectral lines can be used simultaneously without the usual disadvantages becoming dominant. The three triplet lines exhibit almost the same sensitivity, so that greater losses in sensitivity and strong curvature of the calibration curve are avoided. Each individual line naturally exhibits much better linearity. Found that sodium, potassium, calcium, magnesium, and phosphate do not cause interferences in the air-acetylene flame. Investigated interferences on the determination of Mn by various constituents of alloys and found no influences due to iron, cobalt, and molybdenum, slight signal depression in the presence of nickel and aluminium, and slight enhancement in the presence of copper.

Reported that even small amounts of silicon depress the Mn signal; they eliminated this interference by adding 200 mg/L Ca (as chloride). [55]

Observed signal suppression in the presence of phosphorus, borate, tungstate, dichromate, silicate, and cyanide. Complexing ligands such as

EDTA, DCTA, and NTA, on the other hand, caused signal enhancement, which was explained by the formation of volatile complexes.

Observed a signal depression in the presence of molybdenum and rhenium which they attributed to the formation of heteropoly anions which trap Mn in the lattice. Various complexing agents, such as sulfosalicylic acid, help to prevent such interferences. Such interference can also be avoided by using the nitrous oxide-acetylene flame; the characteristic concentration in this flame is about 0.3 mg/L.[3]

1.5.4 Chromium:

Chromium constitutes an estimated 0.02% of the Earth's crust and is therefore among the more common elements. In nature Cr is virtually only found in the form of its compounds. The most important Cr ore is chromite, (Fe, Mn) Cr_2O_4. Chromium is used mostly for the production of stainless steel and chromium alloys, for chromizing and for chromium plating. Chromium (III) is an essential trace element and plays a significant role in glucose metabolism. Compounds of toxic significance are Cr(VI) compounds, and especially Cr(V1) oxide and alkali metal chromates. The stability of aqueous Cr solutions has been the subject of numerous papers.[56]

Although acidification with nitric acid to a pH value < 1.5 can be recommended for the storage of samples for the determination of the total Cr content. Chromium can be determined in both a fuel-rich air-acetylene flame and a nitrous oxide-acetylene flame. The better sensitivity is attained in the former, but the determination is much more subject to interferences. Moreover, Cr (III) and Cr (VI) exhibit different sensitivities in a reducing air-acetylene flame. The addition of 20 g/L ammonium chloride 4 g/L potassium thiocyanate, 20 g/L potassium persulfate, or also 10 g/L ammonium hydrogen fluoride, either alone or together with 2 g/L sodium sulfate, to all measurement solutions has been proposed to eliminate this effect.[57, 58]

More recently organic additives such as amines have also been used successfully. Addition of potassium is recommended for determinations in complex matrices. Chromium exhibits a multitude of analytical lines of similar sensitivity; the line at 357.9 nm is used for most determinations. At this line the characteristic concentration in a fuel-rich air-acetylene flame is 0.04 mg/L. In the nitrous oxide-acetylene flame a characteristic concentration of about 0.3 mg/L can be attained at the 357.9 nm line. The line at 425.4 nm with a characteristic concentration of 0.1 mg/L is more suitable for the determination of higher concentrations of Cr.[3]

1.6 Aim of the work:

The aim of this work is to compare the critical instrumental parameters such as burner height and fuel-oxidant stoichiometry during the analysis of metal ions in a standard solution and in presence of some matrices.

Second step to study the effect of addition of releasing agents and some additives on the absorption signal of the metal ions in presence of some highly interfering matrices such as sodium chloride, urine and serum.

Finally is to study the effect of the sample pretreatment at different temperatures before caring out instrumental analysis.

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CHAPTER (2)
EXPERMENTAL

2.1 Instruments:

2.1.1 Atomic Absorption Spectrometer:

A double beam atomic absorption spectrometer (type Analytic Jena novAA350) with deuterium lamp as continuous source background correction, grating, monochromator and PMT as detector.

Hollow-cathode lamps for Chromium, Cadmium, Nickel and Manganese were used. The working conditions recommended by the manufacturer (Pt/Rh nebulizer, impact bead spoiler and air/acetylene flame) were adhered to. The instrumental parameters for analysis are presented in Table (2.1).

Table (2.1): The parameters of FAAS

Element / Parameter	Cr	Cd	Ni	Mn
Wavelength (nm)	**357.9**	**228.8**	**232.0**	**279.5**
Slit width (nm)	**0.2**	**1.4**	**0.2**	**0.2**
Current (mA)	**4**	**2**	**3**	**5**

2.1.2 Other Instruments:

The thermoregulated **water bath** made by bibby sterilin ltd **Analytical balance** model Mettle Toledor. Single beam **UV/Vis spectrophotometer** Libra S50 made by biochrom ltd. **pH meter** made by Jenway, **Drying oven** made by Gallenkamp.

2.2 Chemicals:

All chemicals used in this study were analar grade. FAAS stock standard solutions 1000 ml/L used from BDH ltd. and PARK ltd. Buffer solutions pH 7.8, 9 and 10 from CORNING ltd. Deionized water 0.05 μs from North Benghazi Station for energy in Alkwfia.

2.3 Precautions against contamination:

For analysis of trace level of analytes, it is necessary to keep the blank values as low as possible. Hence glassware should be cleaned and dried in such a manner to ensure that contamination from glassware does not occur.

The cleaning of glassware and the cleanliness of the environment in which the analysis was performed has a direct effect on the accuracy and precision of the method. In order to achieve accurate results, all glassware was digested and must be cleaned immediately before use, with dilute HCl (1:1) and then rinsed with deionized water.[59]

2.4 Preparation of artificial samples:

2.4.1 Different sodium chloride solutions:

By dissolving 5, 10, 15, 20 and 25g of sodium chloride in deionized water to produce 5, 10, 15, 20 and 25 % of sodium chloride,[60] figure (2.1) shows UV-Vis spectrum for 5 % NaCl solution.

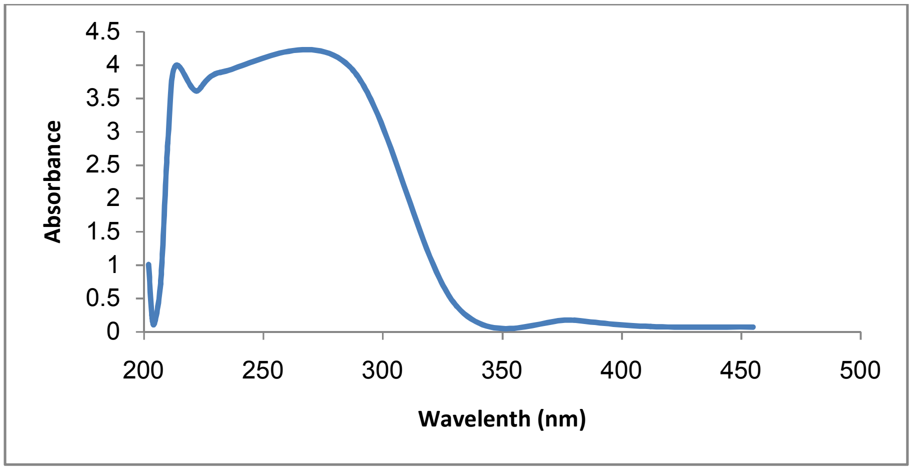

Figure (2.1): UV-Vis spectrum for 5 % NaCl solution

2.4.2 Artificial urine solution:

An artificial urine solution was prepared according to the recipe provided by Brooks and Keevil.[61] The artificial urine solution contained 0.1g lactic acid, 0.96g citric acid, 6.625g $NaHCO_3$, 25.525g urea, 0.9175g CaCl, 13.15g NaCl, 1.23g $MgSO_4$, 3.55g $NaSO_4$, 6.25g K_2HPO_4, and 3.35g NH_4Cl all mixed in 1 L deionized water, figure (2.2) shows UV-Vis spectrum for artificial urine solution.

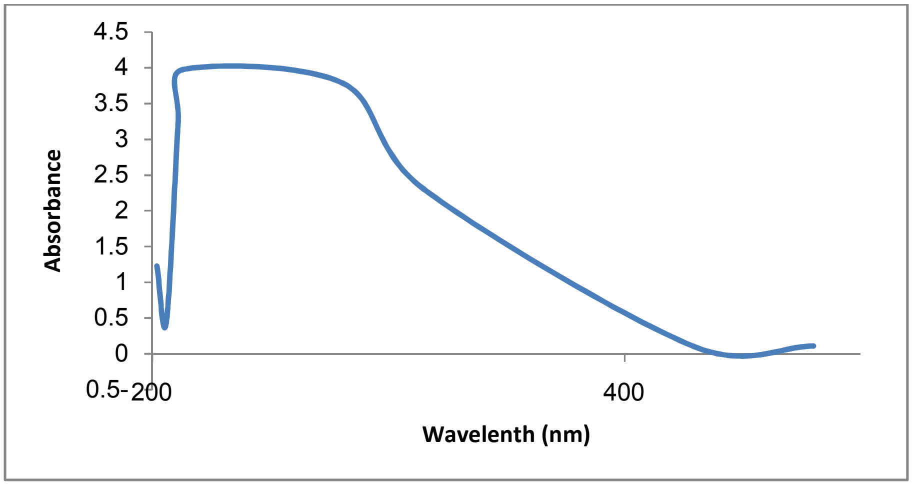

Figure (2.2): UV-Vis spectrum for artificial urine solution.

2.4.3 Artificial serum solution:

Artificial serum was prepared by dissolving 4.037 g NaCl, 0.109 g KCl, 0.100 g KH_2PO_4, 0.185 g $CaCl_2.2H_2O$, and 0.129 g $MgSO_4.7H_2O$ in 500 ml deionized water [62], figure (2.3) shows UV-Vis spectrum for artificial serum solution.

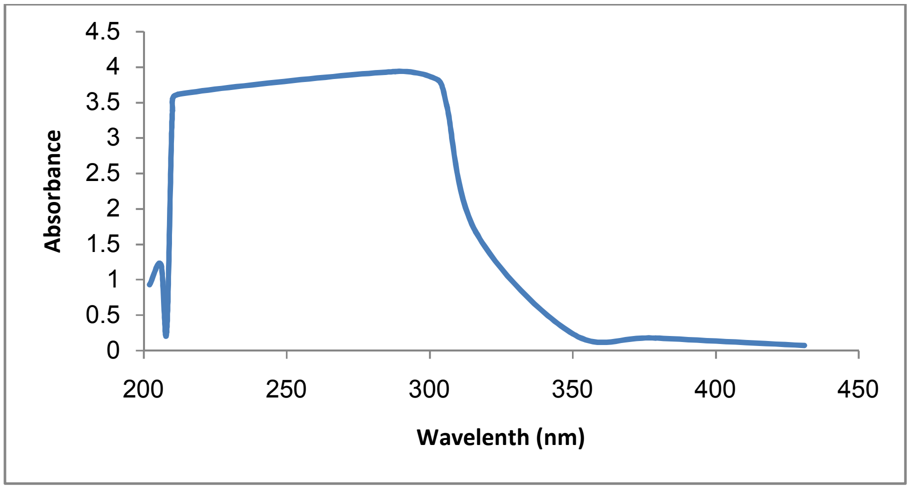

Figure (2.3): UV-Vis spectrum for artificial serum solution.

2.4.4 Other regent:

Absolute ethanol diluted to 8% from MG ltd, 0.01M EDTA from RIEDEL-DE HAEN AG ltd and 5% citric acid from MG ltd.

CHAPTER (3)

RESULTS AND DISCUSSION

3.1 Optimization of instrument parameters:

3.1.1 Effect of fuel-Oxidant Stoichiometry and burner height on Absorbance of Chromium in standard solutions:

The effects of fuel – oxidant Stoichiometry (l/h) and burner height (mm) for chromium ion in standard solution in 0.2 % nitric acid are shown in figures (3.1.a and 3.1.b), as the fuel – oxidant Stoichiometry increase the absorbance of chromium increases; up to maximum value, and then start decreasing. With burner height the absorbance value of chromium also increases, up to maximum, and then decreases with increasing in burner height.

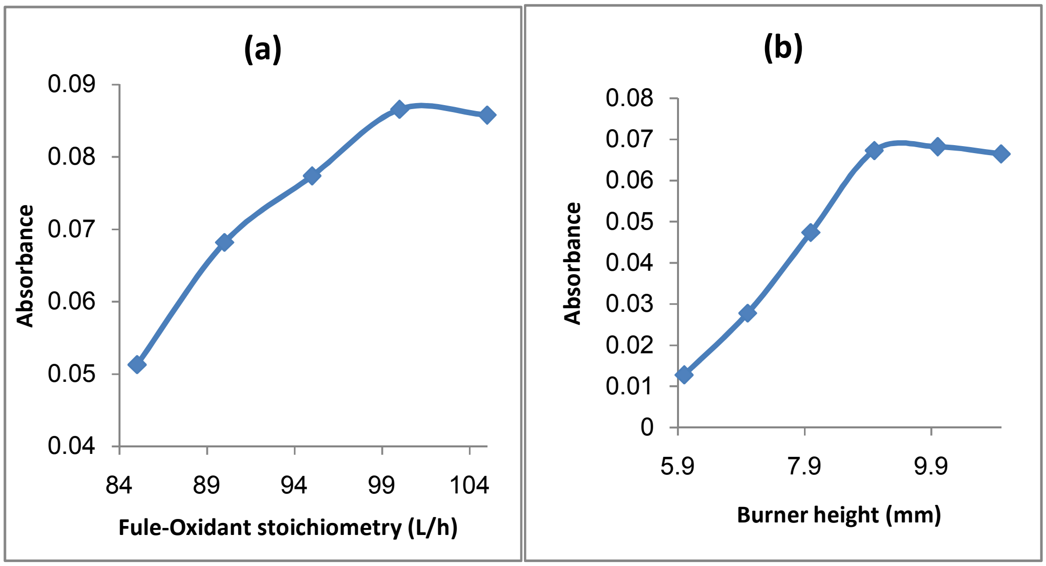

Figure (3.1): The effect of two parameters on absorbance signal of 2 ppm Cr (a): effect fuel-oxidant Stoichiometry at burner height 10 (b): effect of burner height at fuel-oxidant Stoichiometry 90.

3.1.2 Effect of fuel-Oxidant Stoichiometry and burner height on Absorbance of Manganese in standard solutions:

When fuel flow increases the absorbance increases; up to maximum value, followed by sharp decrease in absorbance values.

The increases of burner height up to maximum then going street with absorbance value, the result shown in figure (3.2.a and 3.2.b).

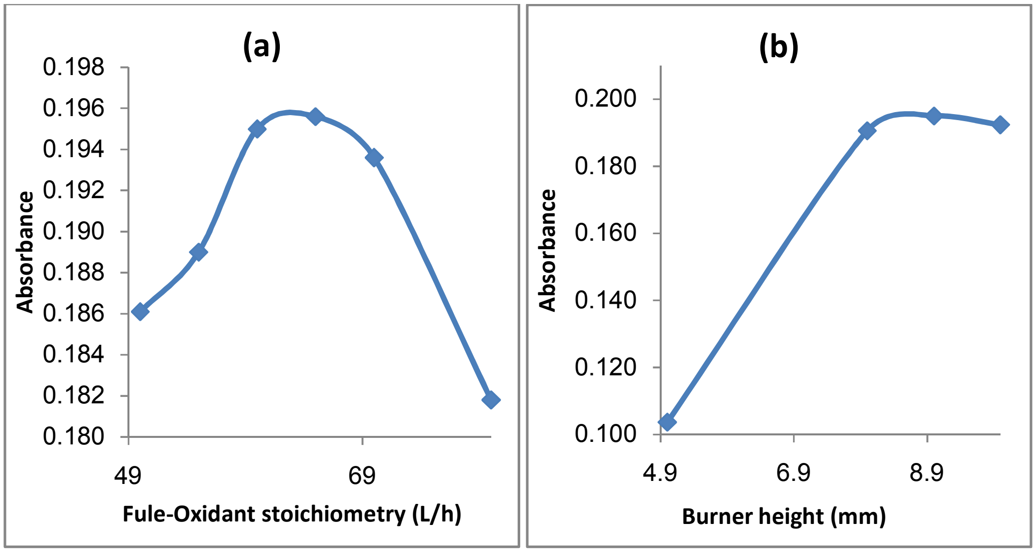

Figure (3.2): The effect of two parameters on absorbance signal of 2 ppm Mn (a): effect fuel-oxidant Stoichiometry at burner height 9 (b): effect of burner height at fuel-oxidant Stoichiometry 60.

3.1.3 Effect of fuel-Oxidant Stoichiometry and burner height on Absorbance of Cadmium in standard solutions:

No change in absorbance with fuel flow till 50 (L/h) then decreases. On the other hand the burner height increases the absorbance increases up to certain point then decreases, the result shown in figure (3.3.a and 3.3.b).

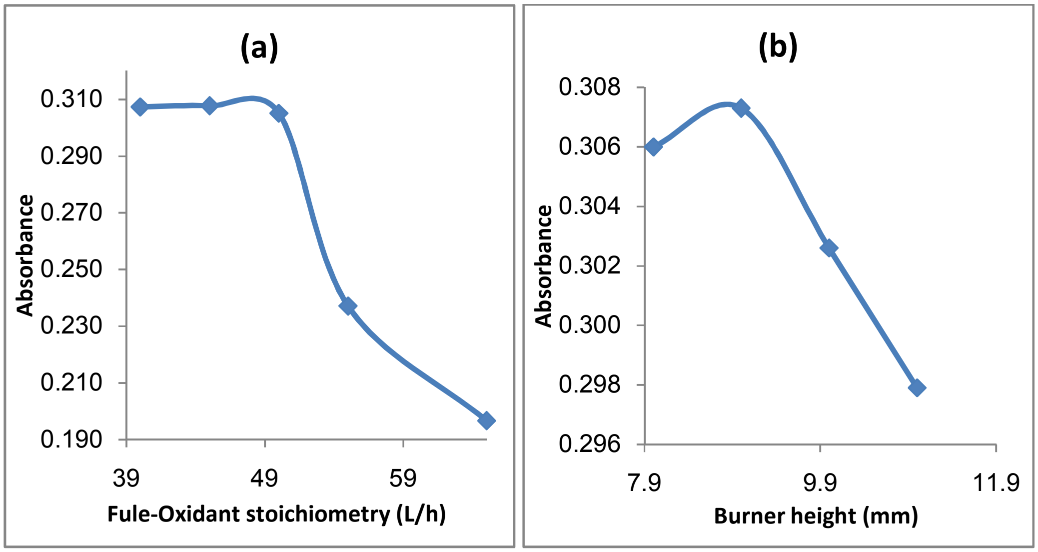

Figure (3.3): The effect of two parameters on absorbance signal of 2 ppm Cd (a): effect fuel-oxidant Stoichiometry at burner height 9 (b): effect of burner height at fuel-oxidant Stoichiometry 40.

3.1.4 Effect of fuel-Oxidant Stoichiometry and burner height on Absorbance of Nickel in standard solutions:

Slight increases in absorbance with fuel flow up to maximum value then decreases. With the increases burner height the absorbance increases up to certain point then decreases. The result shown in figure (3.4.a and 3.4.b)

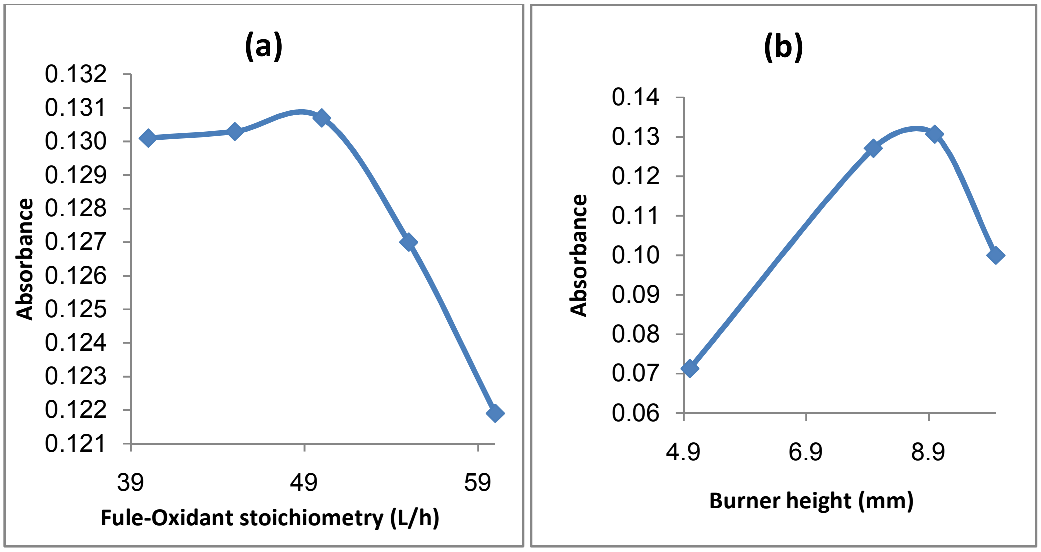

Figure (3.4): The effect of two parameters on absorbance signal of 2 ppm Ni (a): effect fuel-oxidant Stoichiometry at burner height 9 (b): effect of burner height at fuel-oxidant Stoichiometry 50.

3.2 Analysis of metal ions in presence of different sodium chloride concentrations:

3.2.1 Effect of Sodium chloride matrix on absorbance signal of metals:

The effects of different concentrations of sodium chloride matrix on the absorption signal of some metal ions compared with the absorption signal of the same metal ions in a standard solution are shown in figure (3.5). As can be seen from the figure (3.5), the absorbance value (no. of free atoms in gaseous state) is strongly reduced by 40 % in case of Cadmium in presence of 5 % NaCl (sea water) compared with stranded solution with no addition. The reduction of the signal continue with increasing sodium chloride concentration, this means that as concentration of sodium chloride increase the absorption read by the instrument is erroneous and the interference becomes more and more. Manganese and chromium are also affected almost the same as cadmium and the reduction of signal is about 50 % as compared with their standard solutions. Nickel which is known as less volatile element showed a stable absorption values at 5 % sodium chloride solution and a slight decrease in of absorption at 10 % matrix concentration.

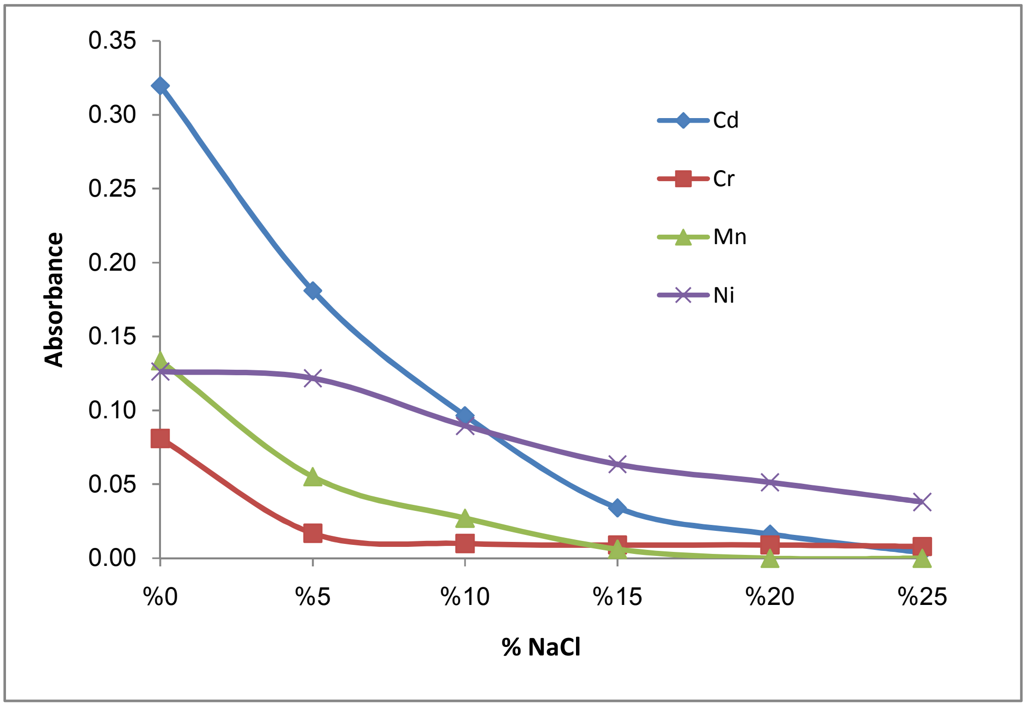

Figure (3.5): Effect of different sodium chloride concentrations matrix on the absorption signal some trace elements

3.2.2 Optimization of cadmium analysis in presence of 5 % sodium chloride:

Optimization of cadmium analysis in presence of sodium chloride matrix is investigated using a standard solution of 2 ppm Cd in 5 % NaCl, the results obtained for fuel-oxidant Stoichiometry and burner height are shown in figures (3.6.a and 3.6.b) respectively.

Better absorption values could be obtained at 40 fuel oxidant and burner height of 7mm instead of 40 and 9 mm for cadmium in case of standard solution.

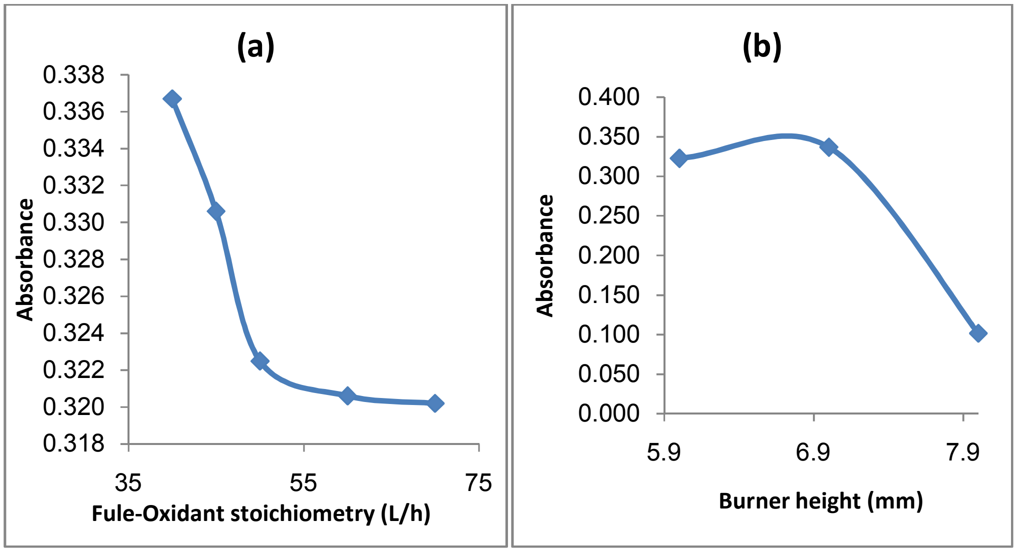

Figure (3.6): The effect of two parameters on absorbance signal of cadmium analysis in presence of 5% sodium chloride (a): effect of fuel-oxidant stoichiometry at burner height 7 (b): effect of burner height at 40 fuel-oxidant stoichiometry.

3.2.3 Effect of some additives on absorption of cadmium in sodium chloride matrix:

The effects of some additives such as releasing agents on the absorption signal of cadmium in sodium chloride matrix and compared to that value in case of standard solution at different temperatures are investigated. Results obtained at room temperature are shown in figure (3.7). As can be seen from the figure below that sodium chloride reduces the absorption signal of cadmium, slight enhancement for absorption signal in case of adding EDTA as releasing agent, a very good effect is shown by addition of ethanol and more reduction in signal is obtained in case of citric acid addition.

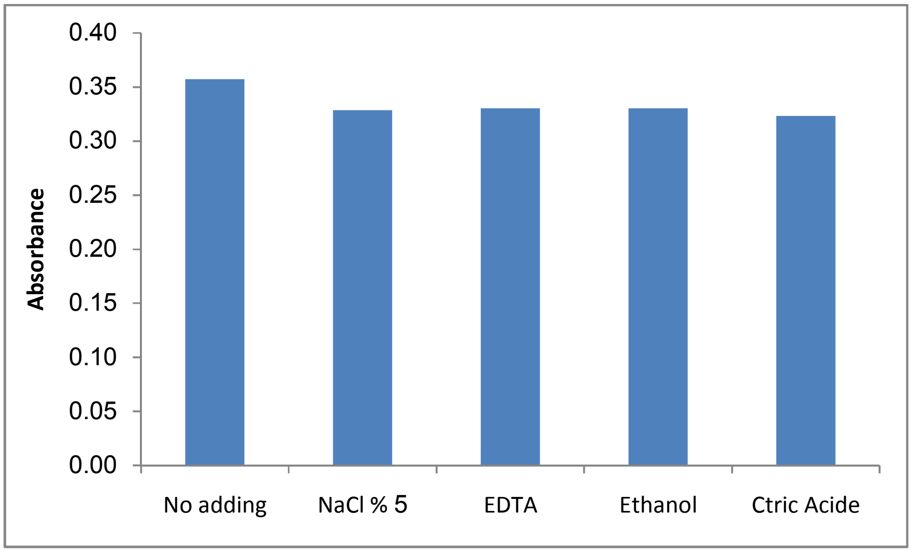

Figure (3.7): Absorbance of 2ppm Cd in 5% NaCl matrix with different additives at room temperature.

Figures (3.8 and 3.9) show the effect of addition of some releasing agents to 2 ppm cadmium solution in presence of 5 % sodium chloride matrix at 50 and 80^{0}C. From the figures below, better enhancement for absorption signal in all cases at higher temperatures.

With ethanol the signal becomes even better than that for the standard solution which is mentioned by welz.

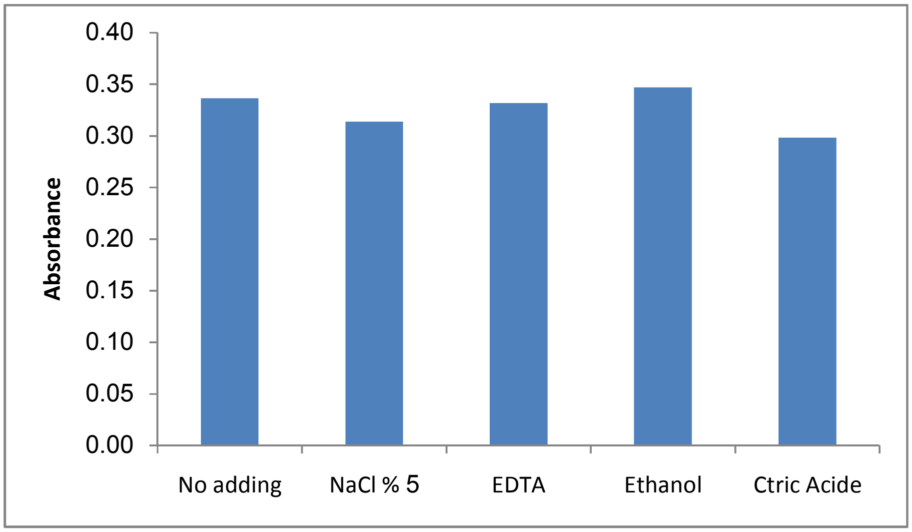

Figure (3.8): Absorbance of 2ppm Cd in 5% NaCl matrix with different additives at 50^{0}C.

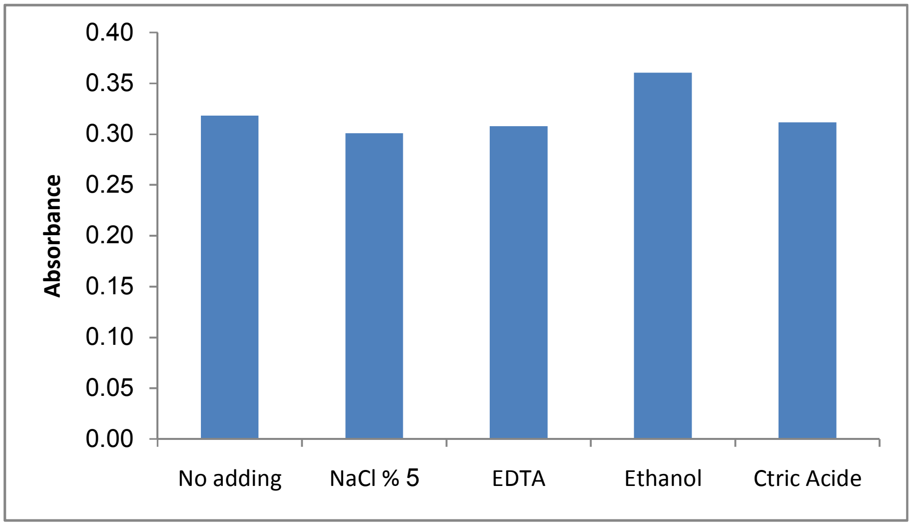

Figure (3.9): Absorbance of 2ppm Cd in 5% NaCl matrix with different additives at 80^{0}C.

3.2.4 Optimization of fuel-oxidant Stoichiometry and burner height for Nickel in 5 % sodium chloride matrix:

Optimization of Nickel analysis in presence of sodium chloride matrix is investigated using a standard solution of 2 ppm Ni in 5 % NaCl. The results obtained for fuel-oxidant Stoichiometry and burner height are shown in figures (3.10.a and 3.10.b) respectively.

Better absorption values could be obtained at 60 fuel oxidant burner and 8 mm height of instead of 50 and 9 mm for Nickel in case of standard solution.

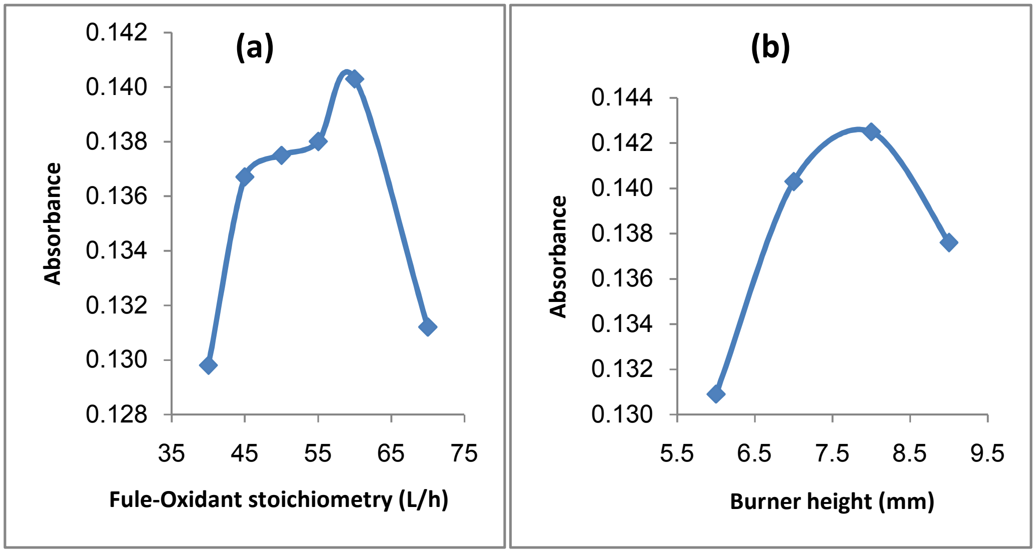

Figure (3.10): The effect of two parameters on absorbance signal of nickel analysis in presence of 5% sodium chloride (a): effect of fuel-oxidant stoichiometry at burner height 7 (b): effect of burner height at 60 fuel-oxidant stoichiometry.

3.2.5 Effect of some additives on absorption of Nickel in sodium chloride matrix:

The effects of some additives such as releasing agents on the absorption signal of Nickel in sodium chloride matrix are investigated and compared that of standard solution at different temperatures. Results obtained at room temperature are shown in figure (3.11). As can be seen from the figure below sodium chloride reduces the absorption signal of cadmium, more reduction in signal is obtained in case of adding EDTA as releasing agent, a very good effect is shown by addition of ethanol and more reduction in signal is obtained in case of citric acid addition.

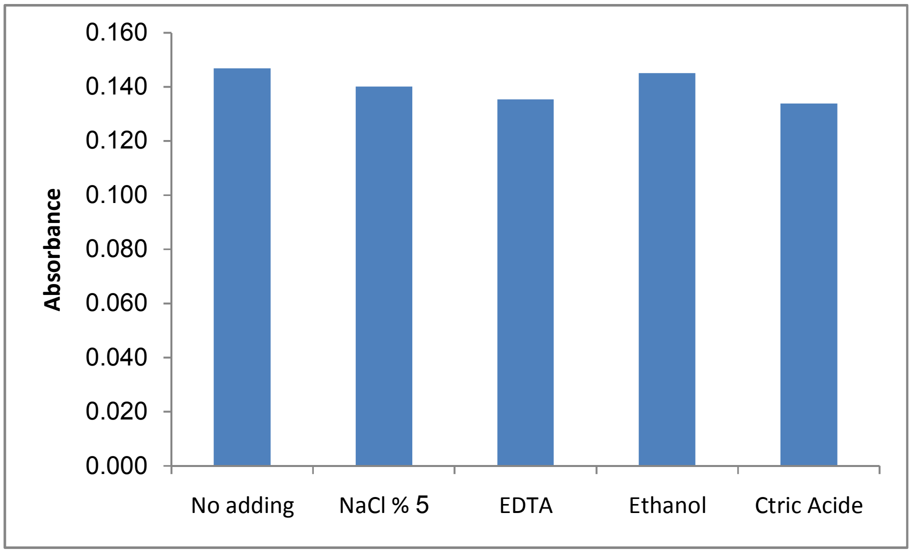

Figure (3.11): The absorbance of 2ppm Ni in 5 % NaCl with different additives at room temperature.

Figures (3.12 and 3.13) below show the effect of addition of some releasing agents to 2 ppm Nickel solution in presence of 5 % sodium chloride matrix at 50 and 80^{0}C, from the figures below better enhancement for absorption signal in all cases at higher temperatures, with ethanol the signal becomes even better than that of the standard solution.

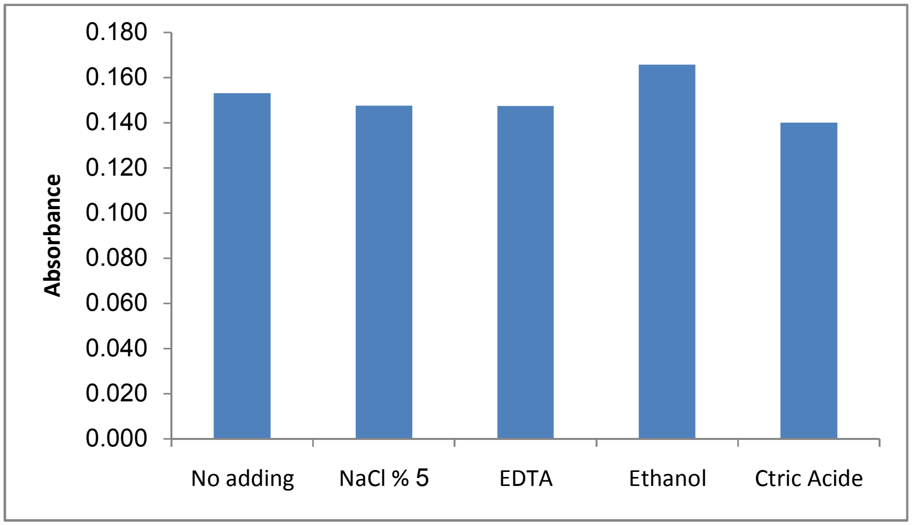

Figure (3.12): The absorbance of 2ppm Ni in 5 % NaCl with different additives at 50^{0}C.

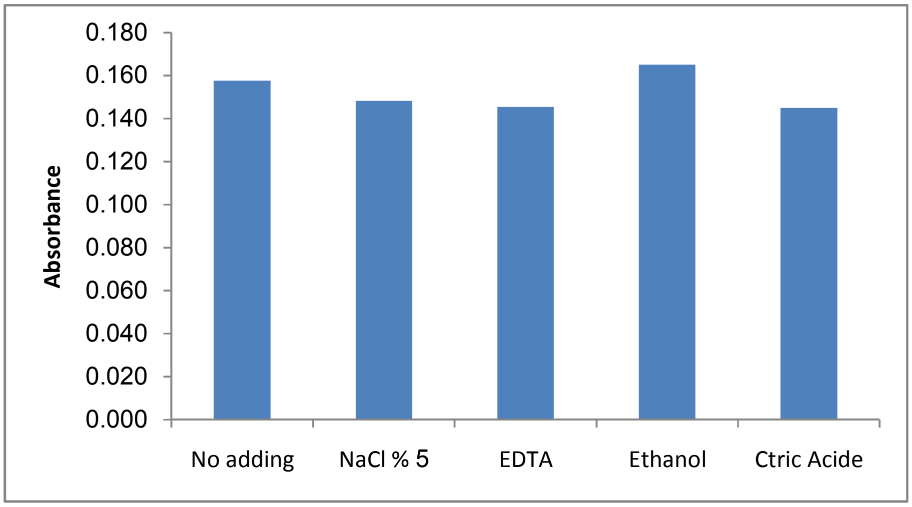

Figure (3.13): The absorbance of 2ppm Ni in 5 % NaCl with different additives at 80^{0}C.

3.2.6 Optimization of fuel-oxidant Stoichiometry and burner height for Chromium in 5 % sodium chloride matrix:

Optimization of Chromium analysis in presence of sodium chloride matrix is investigated using 2 ppm Cr in 5 % NaCl, the results obtained for fuel-oxidant Stoichiometry and burner height are shown in figures (3.14.a and 3.14.b) respectively. Better absorption values could be obtained at 80 fuel oxidant and 9 mm burner height instead of 100 and 10 mm for Nickel in case of standard solution.

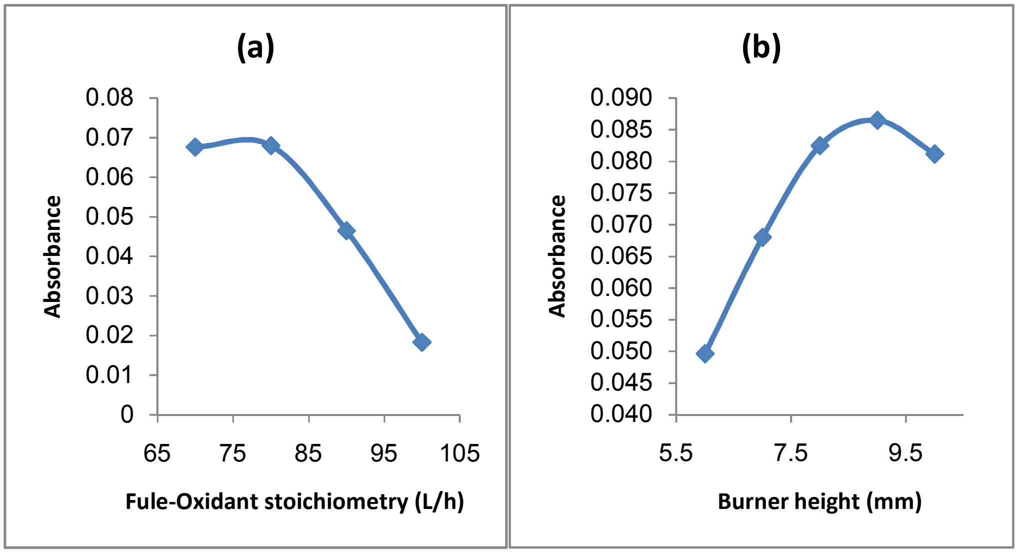

Figure (3.14): The effect of two parameters on absorbance signal of chromium analysis in presence of 5% sodium chloride (a): effect of fuel-oxidant stoichiometry at burner height 7 (b): effect of burner height at 80 fuel-oxidant stoichiometry.

3.2.7 Effect of some additives on absorption of Chromium in sodium chloride matrix:

The effects of some additives such as releasing agents on the absorption signal of Chromium in sodium chloride matrix are investigated and compared with that of standard solution at different temperatures. Results obtained at room temperature are shown in figure (3.15). As can be seen from the figure below that sodium chloride reduces the absorption signal of Chromium, and the signal becomes slightly better in case of adding EDTA as releasing agent, and better effect can be shown by addition of ethanol and citric acid addition.

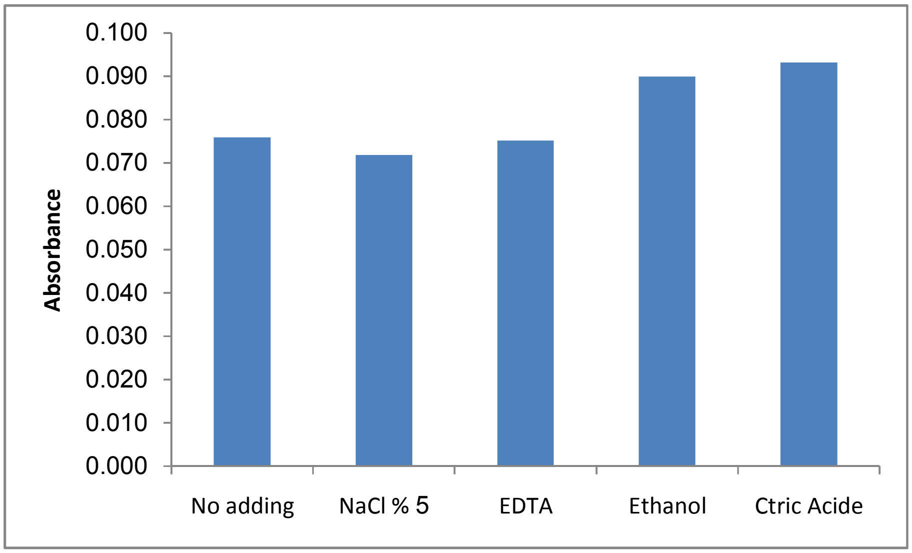

Figure (3.15): The absorbance of 2ppm Cr in 5 % NaCl with different additives at room temperature.

Figures (3.16 and 3.17) below show the effect of addition of some releasing agents to 2 ppm Chromium solution in presence of 5 % sodium chloride matrix at 50 and 80°C. From the figures below, better enhancement for absorption signal in all cases at higher temperatures. With citric acid, the signal becomes even better than that for the standard solution.

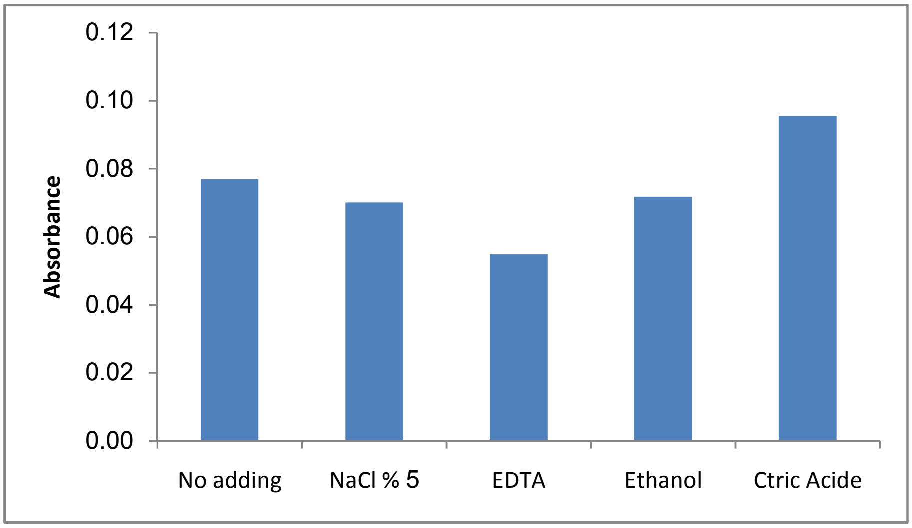

Figure (3.16): The absorbance of 2ppm Cr in 5 % NaCl with different additives at 50^0C.

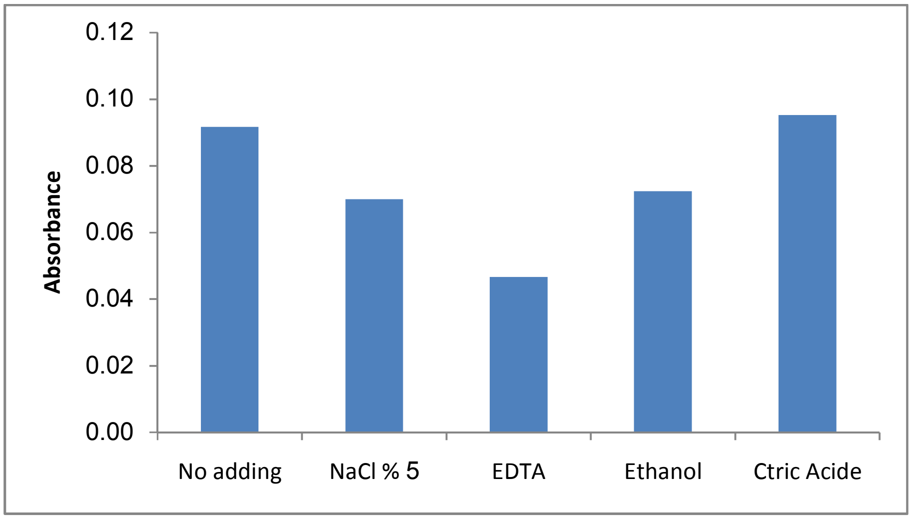

Figure (3.17): The absorbance of 2ppm Cr in 5 % NaCl with different additives at 80^0C.

3.2.8 Optimization of fuel-oxidant Stoichiometry and burner height for Manganese in 5 % sodium chloride matrix:

Optimization of Manganese analysis in presence of sodium chloride matrix is investigated using a standard solution of 2 ppm Mn in 5 % NaCl. The results obtained for fuel-oxidant Stoichiometry and burner height are shown in figures (3.18.a and 3.18.b) respectively. Better absorption values are obtained at 65 fuel oxidant and 10 mm burner height instead of 60 and 9 mm for Manganese in case of standard solution.

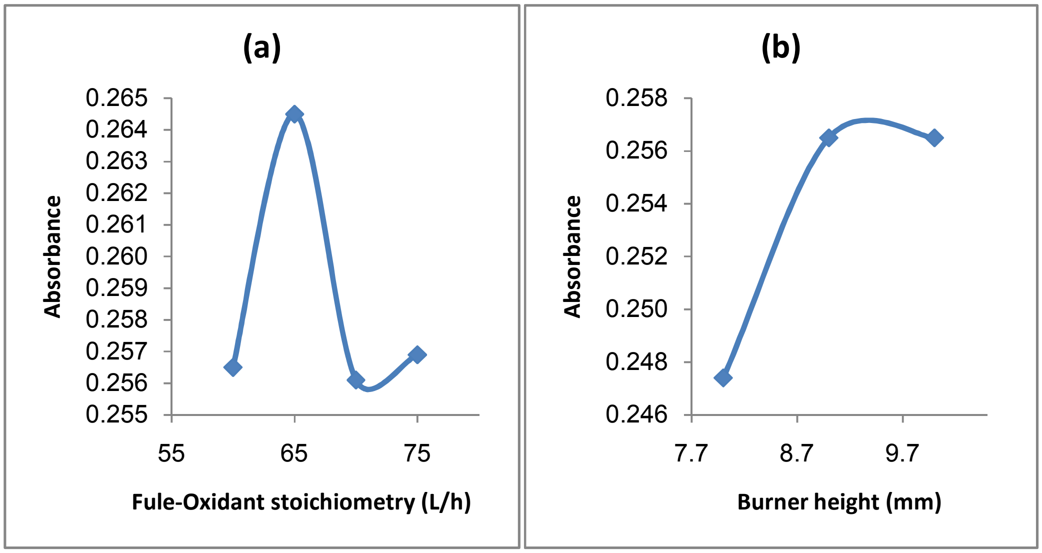

Figure (3.18): The effect of two parameters on absorbance signal of manganese analysis in presence of 5% sodium chloride (a): effect of fuel-oxidant stoichiometry at burner height 9 (b): effect of burner height at 65 fuel-oxidant stoichiometry.

3.2.9 Effect of some additives on absorption of Manganese in sodium chloride matrix:

The effects of some additives such as releasing agents on the absorption signal of Manganese in sodium chloride matrix are investigated and compared with that of standard solution at different temperatures. Results obtained at room temperature are shown in figure (3.19). As can be seen from the figure below, sodium chloride reduces the absorption signal of Manganese, and more reduction in signal is obtained in case of adding EDTA as releasing agent, and reduction in case of addition of ethanol and citric acid addition.

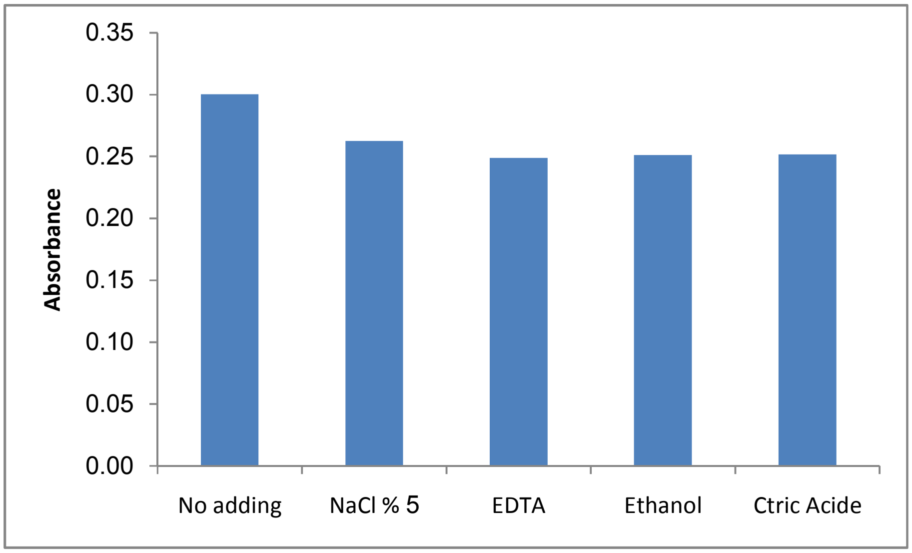

Figure (3. 19): The absorbance of 2ppm Mn in 5 % NaCl with different additives at room temperature.

Figures (3.20 and 3.21) below show the effect of addition of some releasing agents to 2 ppm Manganese solution in presence of 5 % sodium chloride matrix at 50 and 80°C. From the figures below, there is no apparent effect on absorption signal in all cases at higher temperatures.

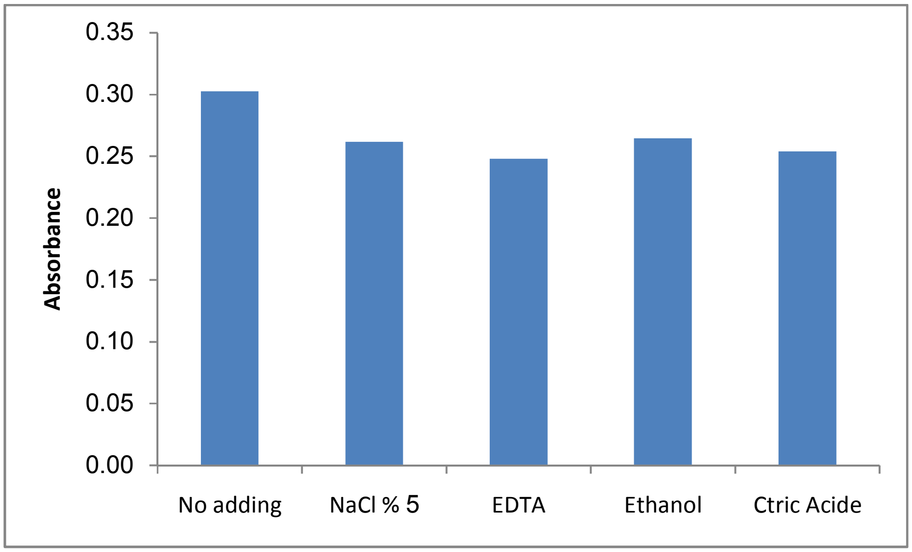

Figure (3.20): The absorbance of 2ppm Mn in 5 % NaCl with different additives at 50^0C

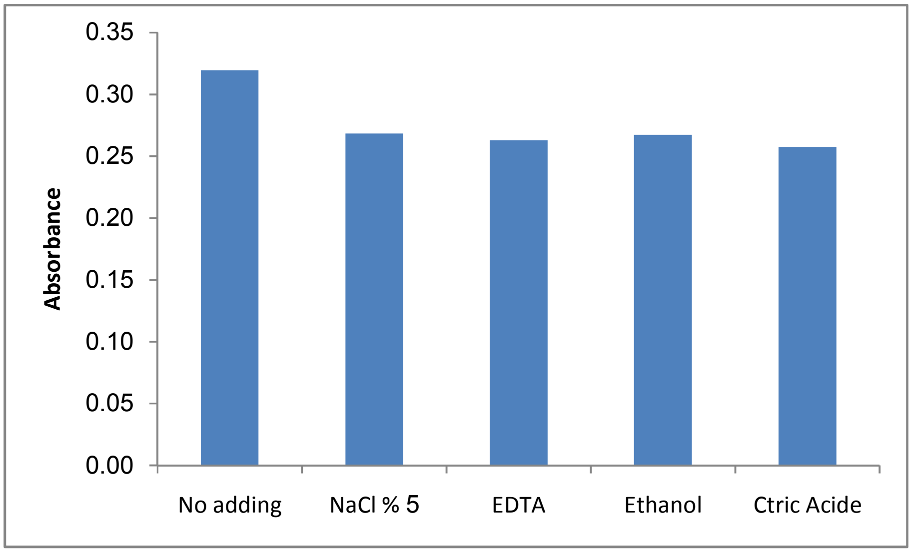

Figure (3.21): The absorbance of 2ppm Mn in 5 % NaCl with different additives at 80^0C.

3.3 Optimization of metals analysis presence in artificial urine solution:

3.3.1 Optimization of cadmium analysis in presence of artificial urine solution:

Optimization of cadmium analysis in presence of artificial urine matrix is investigated using 0.5 ppm Cd in artificial urine solution, the results obtained for fuel-oxidant Stoichiometry and burner height are shown in figures (3.22 a and 3.22 b) respectively. Better absorption values are obtained at 40 fuel oxidant and 7 mm burner height of instead of 40 and 9 mm for standard solution.

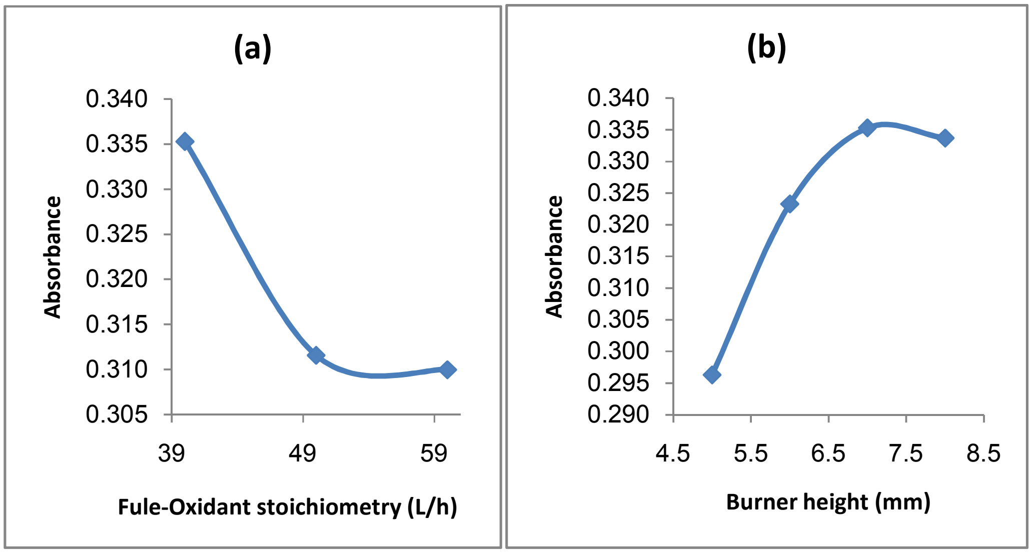

Figure (3.22): The effect of two parameters on absorbance signal of cadmium analysis presence in artificial urine solution (a): effect of fuel-oxidant stoichiometry at burner height 7 (b): effect of burner height at 40 fuel-oxidant stoichiometry.

3.3.2 Effect of some additives on absorption of Cadmium in artificial urine matrix:

The effects of some additives such as releasing agents on the absorption signal of Cadmium in artificial urine matrix are investigated and compared with that of standard solution at different temperatures. Results obtained at room temperature are shown in figure (3.23). As can be seen from the figure below, artificial urine matrix reduces the absorption signal of Cadmium, and good effect on absorption signal as compared with the original standard solution signal is shown by addition of EDTA, and ethanol.

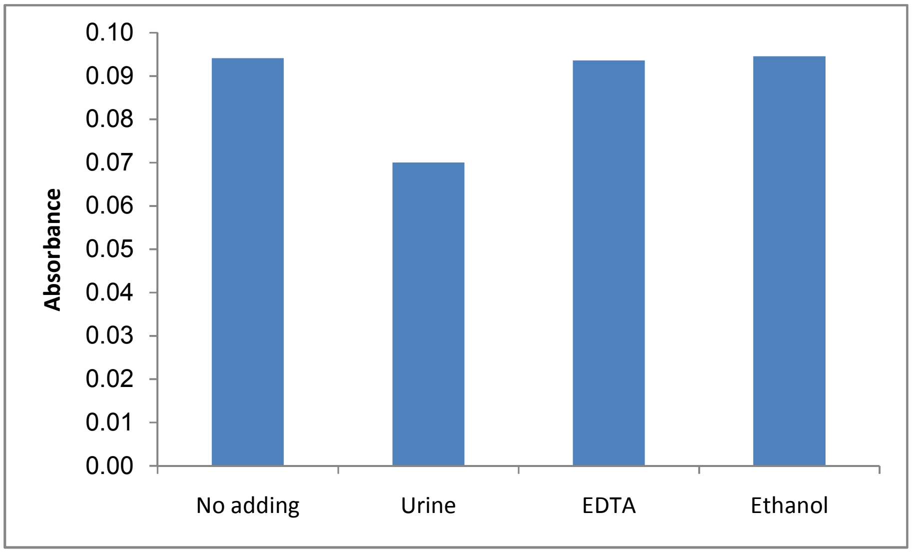

Figure (3.23): The absorbance of 0.5 ppm Cd in artificial urine solution with different additives at room temperature.

Figures (3.24 and 3.25) below show the effects of addition of some releasing agents to 0.5 ppm cadmium solution in presence of artificial urine matrix at 50 and 80^{0}C. From the figures below, better enhancement for absorption signal in all cases at higher temperatures, with ethanol the signal becomes even better than that for the standard solution.

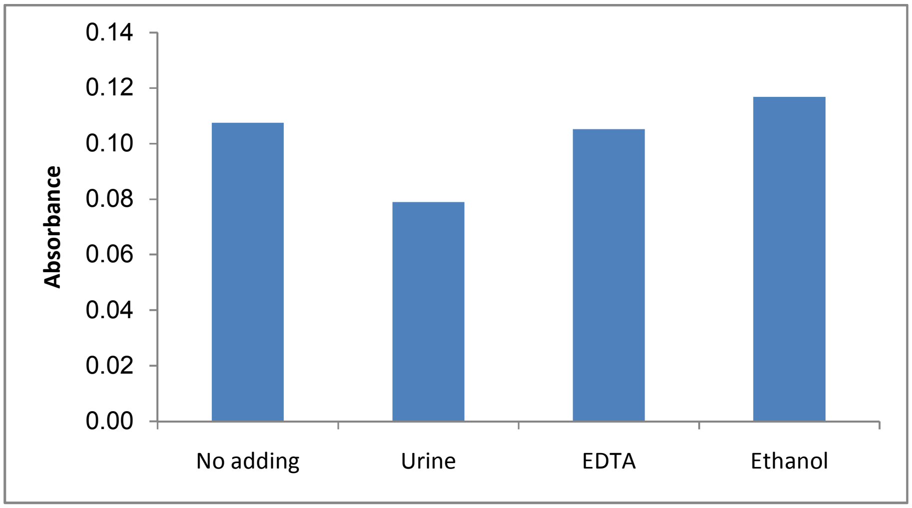

Figure (3.24): The absorbance of 0.5 ppm Cd in artificial urine solution with different additives at 50^{0}C.

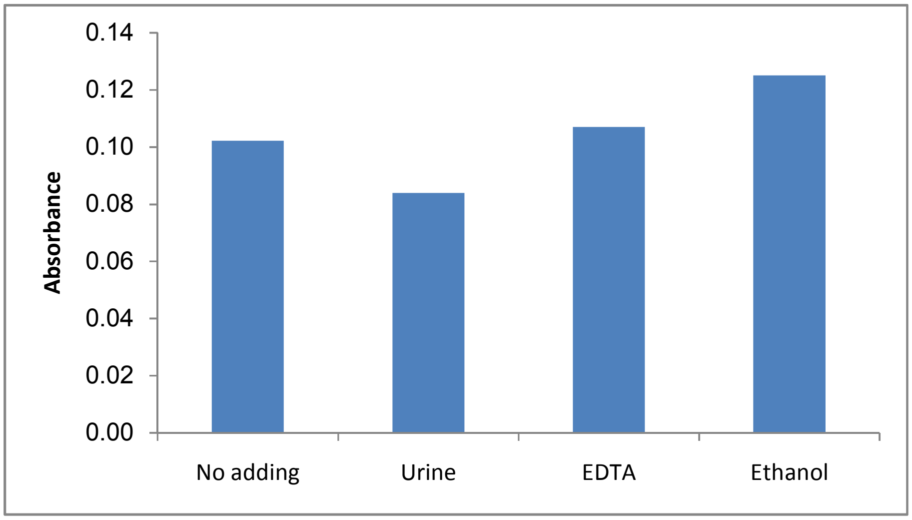

Figure (3.25): The absorbance of 0.5 ppm Cd in artificial urine solution with different additives at 80^0 C.

3.3.3 Optimization of nickel analysis in presence of artificial urine solution:

Optimization of nickel analysis in presence of artificial urine matrix is investigated using of 1 ppm Ni in artificial urine solution , the results obtained for fuel-oxidant Stoichiometry and burner height are shown in figures (3.26 a and 3.26 b) respectively. Better absorption values are obtained at 50 fuel oxidant and 10 mm burner height instead of 50 and 9 mm for standard solution.

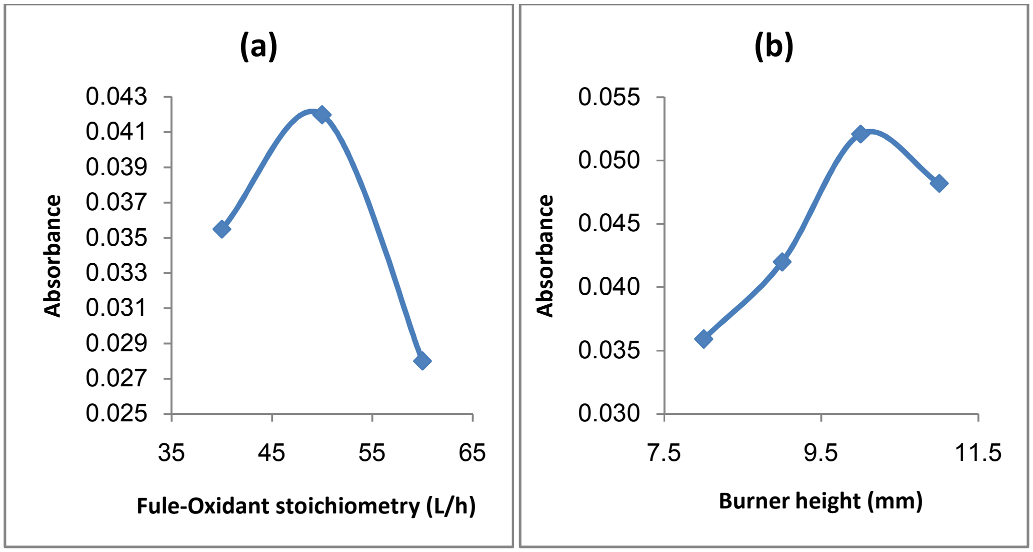

Figure (3.26): The effect of two parameters on absorbance signal of nickel analysis presence in artificial urine solution (a): effect of fuel-oxidant stoichiometry at burner height 9 (b): effect of burner height at 50 fuel-oxidant stoichiometry.

3.3.4 Effect of some additives on absorption of nickel in artificial urine matrix:

The effects of some additives such as releasing agents on the absorption signal of nickel in artificial urine matrix are investigated and compared with that of standard solution at different temperatures. Results obtained at room temperature are shown in figure (3.27). As can be seen from the figure below , that artificial urine matrix reduces the absorption signal of nickel, and more reduction in signal is obtained in case of adding EDTA as releasing agent, addition of ethanol shows relatively better absorption signals than EDTA.

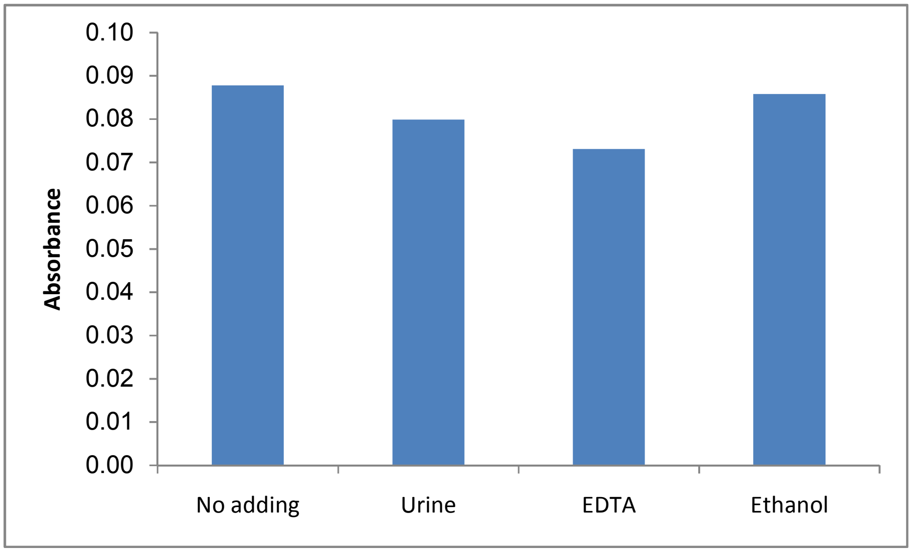

Figure (3.27): The absorbance of 1 ppm Ni in artificial urine solution with different additives at room temperature.

Figures (3.28 and 3.29) below show the effect of addition of some releasing agents to 1 ppm nickel presence of artificial urine matrix at 50 and 80^{0}C. From the figures below, better enhancement for absorption signal in all cases at higher temperatures, with ethanol the signal becomes even better than that for the standard solution.

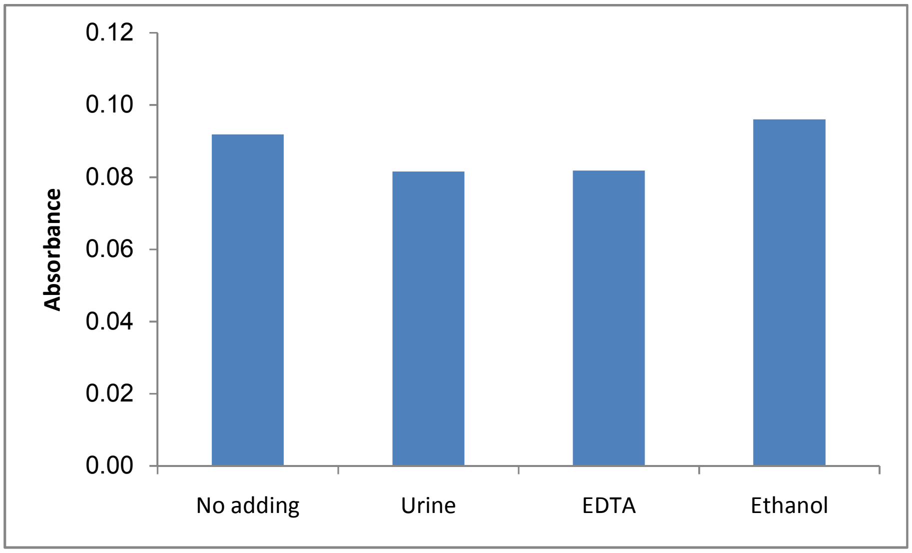

Figure (3.28): The absorbance of 1 ppm Ni in artificial urine solution with different additives at 50^{0}C.

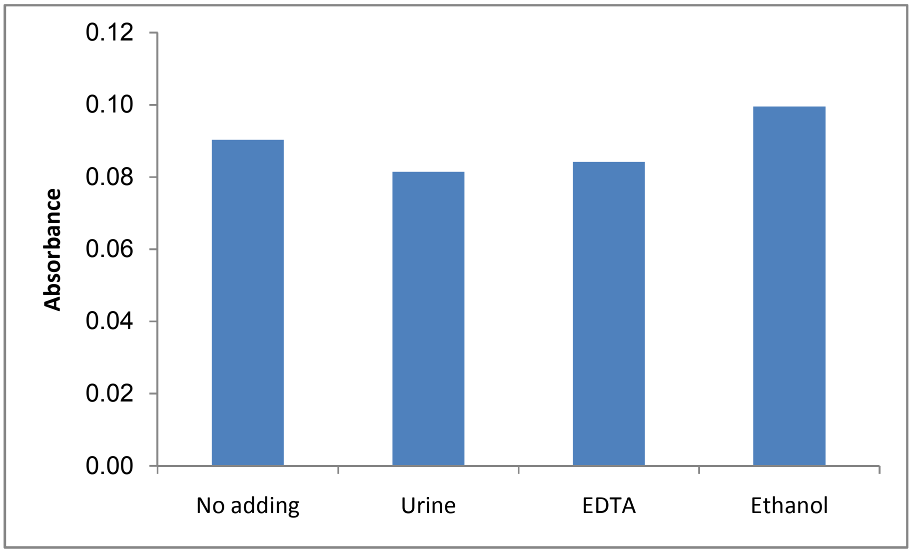

Figure (3.29): The absorbance of 1 ppm Ni in artificial urine solution with different additives at 80^{0}C.

3.3.5 Optimization of chromium analysis in presence of artificial urine solution:

Optimization of chromium analysis in presence of artificial urine matrix is investigated using 1.5 ppm Cr in artificial urine solution , the results obtained for fuel-oxidant Stoichiometry and burner height are shown in figures (3.30 a and 3.30 b) respectively. Better absorption values are obtained at 90 fuel oxidant and 11 mm burner height of instead of 100 and 10 mm for standard solution.

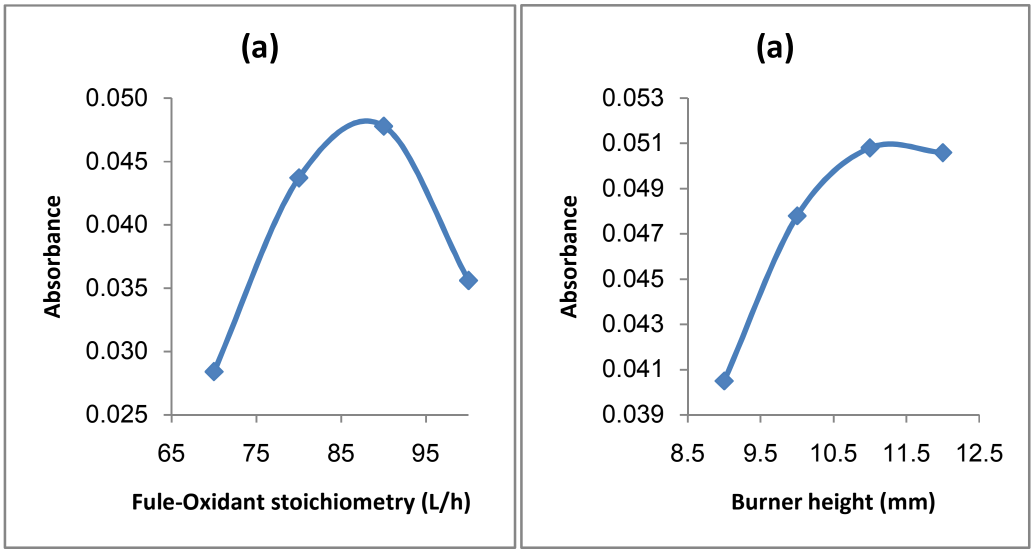

Figure (3.30): The effect of two parameters on absorbance signal of chromium analysis presence in artificial urine solution (a): effect of fuel-oxidant stoichiometry at burner height 10 (b): effect of burner height at 90 fuel-oxidant stoichiometry.

3.3.6 Effect of some additives on absorption of chromium in artificial urine matrix:

The effects of some additives such as releasing agents on the absorption signal of chromium in artificial urine matrix are investigated and compared with that value in case of standard solution at different temperatures. Results obtained at room temperature are shown in figure (3.31). As can be seen from the figure below that artificial urine matrix reduces the absorption signal of chromium, and more absorption in signal is obtained in case of adding EDTA as releasing agent, addition of ethanol is also gives better sensitivity than the signal in matrix without any releasing agent addition.

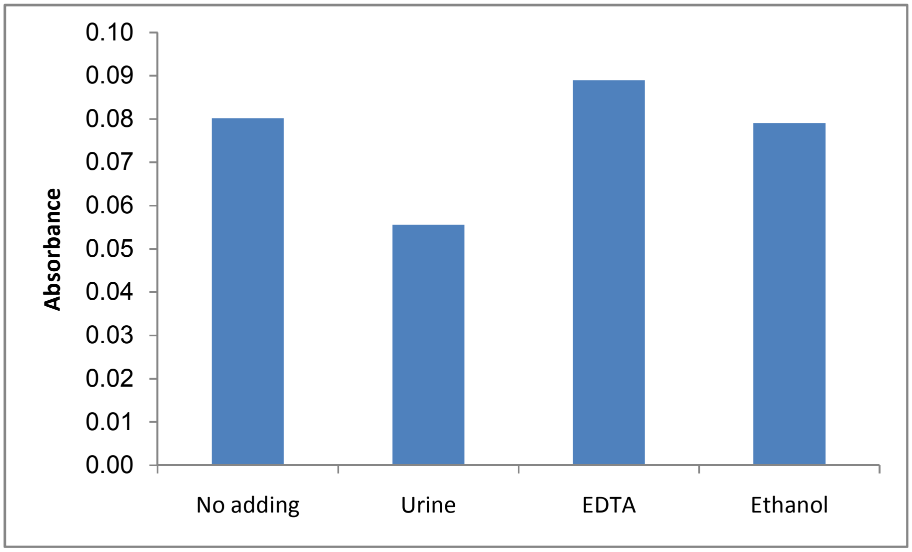

Figure (3.31): The absorbance of 1.5 ppm Cr in artificial urine solution with different additives at room temperature.

Figures (3.32 and 3.33) below show the effect of addition of some releasing agents to 1.5 ppm chromium presence of artificial urine matrix at 50 and 80⁰C. From the figures below, better enhancement for absorption signal in all cases at higher temperatures. Generally EDTA works better with chromium in presence of urine matrix than ethanol.

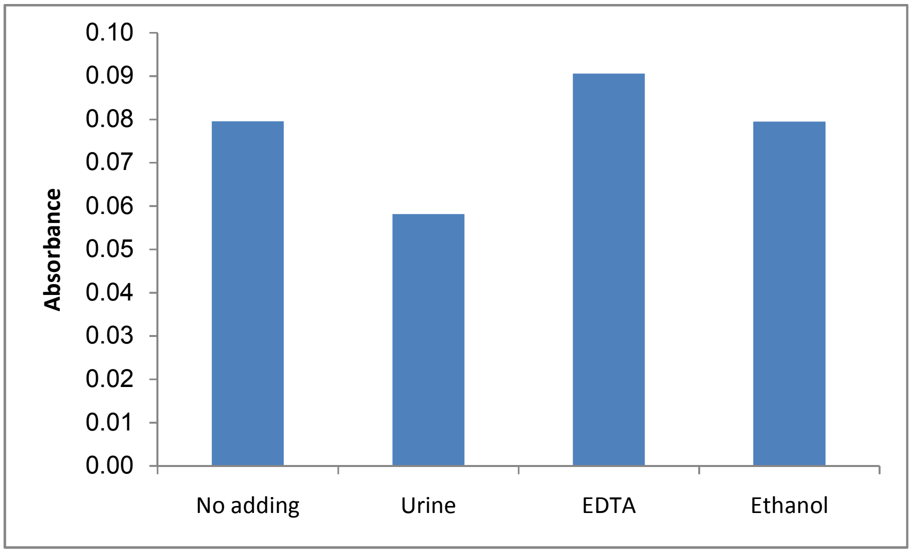

Figure (3.32): The absorbance of 1.5 ppm Cr in artificial urine solution with different additives at 50^{0}C.

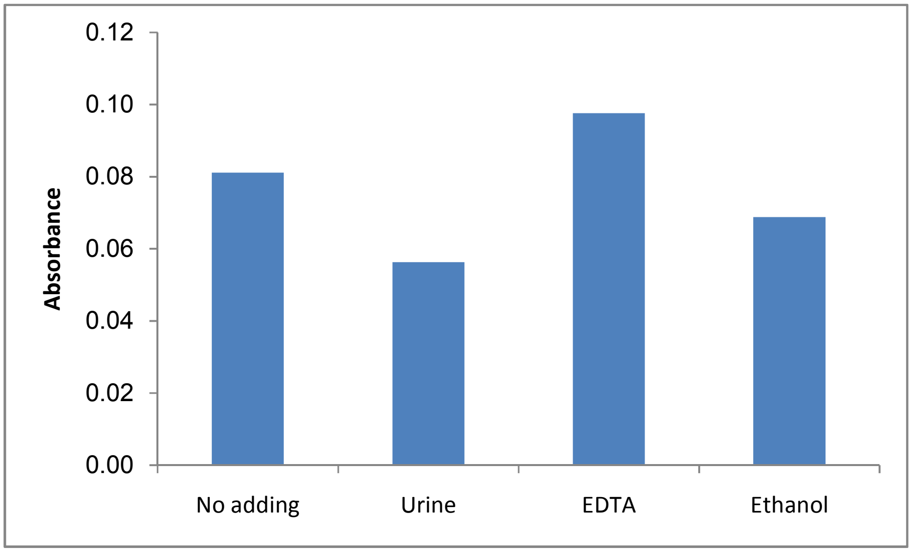

Figure (3.33): The absorbance of 1.5 ppm Cr in artificial urine solution with different additives at 80^0 C.

3.3.7 Optimization of manganese analysis in presence of artificial urine solution:

Optimization of manganese analysis in presence of artificial urine matrix is investigated using 1 ppm Mn in artificial urine solution , the results obtained for fuel-oxidant Stoichiometry and burner height are shown in figures (3.34 a and 3.34 b) respectively. Better absorption values are obtained at 55 fuel oxidant and 12 mm burner height instead of 60 and 9 mm for standard solution.

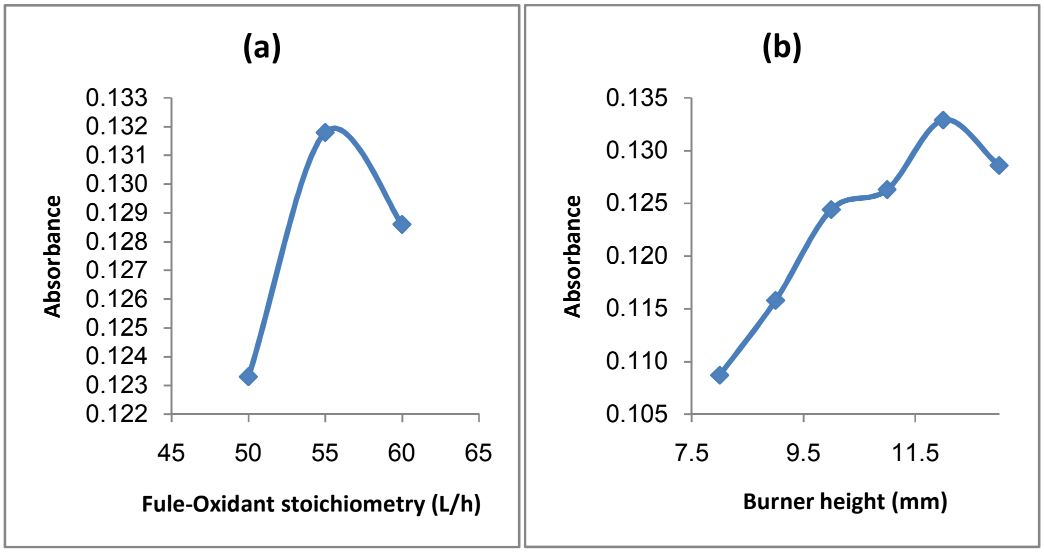

Figure (3.33): The effect of two parameters on absorbance signal of manganese analysis presence in artificial urine solution (a): effect of fuel-oxidant stoichiometry at burner height 12 (b): effect of burner height at 55 fuel-oxidant stoichiometry.

3.3.8 Effect of some additives on absorption of manganese in artificial urine matrix:

The effects of some additives such as releasing agents on the absorption signal of manganese in artificial urine matrix are investigated and compared with that value in case of standard solution at different temperatures. Results obtained at room temperature are shown in figure 3.34. As can be seen from the figure below, artificial urine matrix reduces the absorption signal of manganese, and more reduction in signal is obtained in case of adding EDTA as releasing agent, addition of ethanol enhances the sensitivity of manganese determination as compared with that for manganese in presence of matrix.

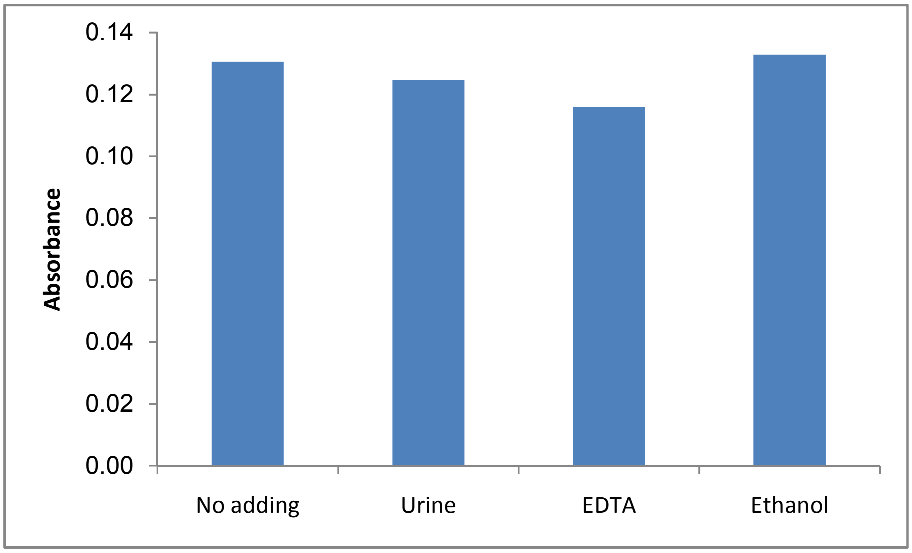

Figure (3.34): The absorbance of 1 ppm Mn in artificial urine solution with different additives at room temperature.

Figures (3.35 and 3.36) below show the effect of addition of some releasing agents to 1 ppm manganese presence of artificial urine matrix at 50 and 80°C. From the figures below, better enhancement for absorption signal in all cases at higher temperatures, with ethanol the signal becomes better.

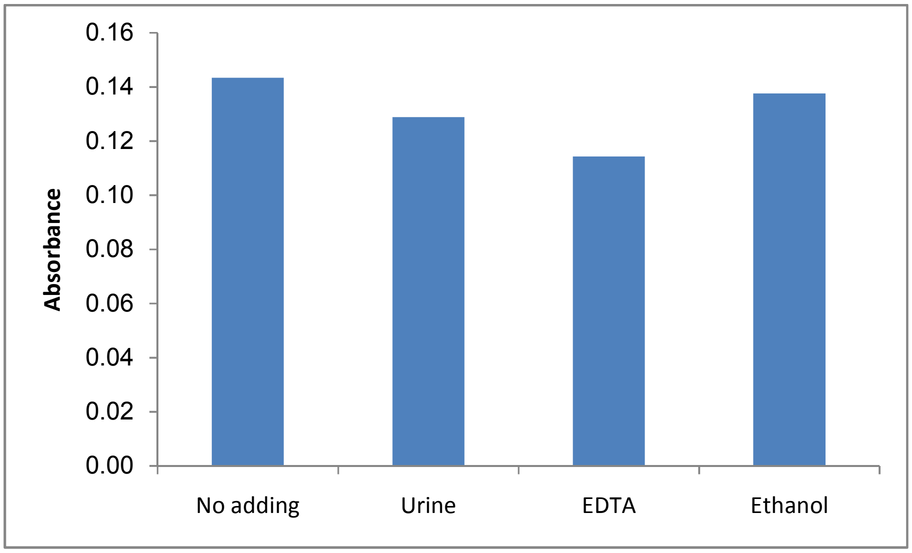

Figure (3.35): The absorbance of 1 ppm Mn in artificial urine solution with different additives at 50°C.

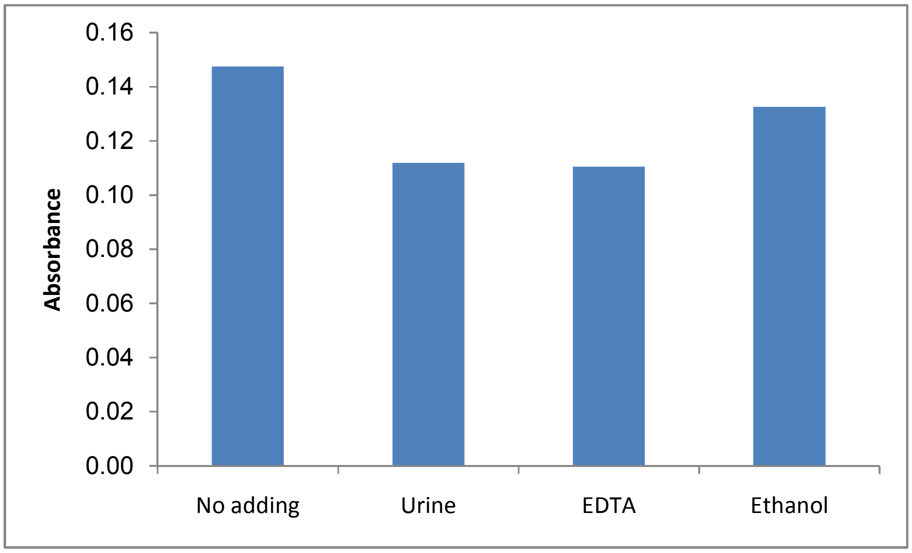

Figure (3.36): The absorbance of 1 ppm Mn in artificial urine solution with different additives at 80°C.

3.4 Optimization of metals analysis in presence of artificial serum solution:

3.4.1 Optimization of cadmium analysis in presence of artificial serum solution:

Optimization of cadmium analysis in presence of artificial serum matrix is investigated using 0.5 ppm Cd in artificial serum solution , the results obtained for fuel-oxidant Stoichiometry and burner height are shown in figures (3.37 a and 3.37 b) respectively. Better absorption values are obtained at 40 fuel oxidant and 7 mm burner height instead of 40 and 9 mm for standard solution.

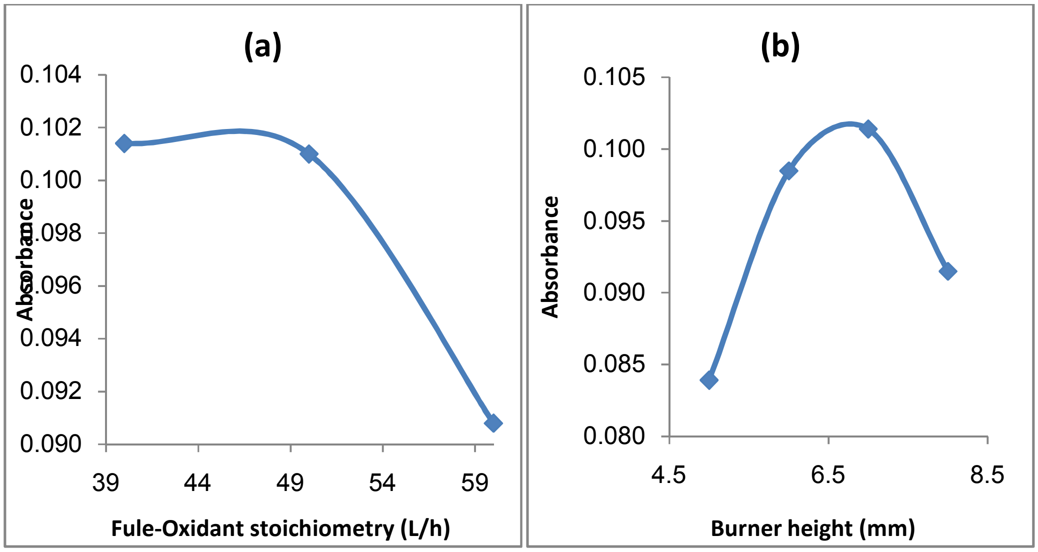

Figure (3.37): The effect of two parameters on absorbance signal of cadmium analysis presence in artificial serum solution (a): effect of fuel-oxidant stoichiometry at burner height 7 (b): effect of burner height at 40 fuel-oxidant stoichiometry.

3.4.2 Effect of some additives on absorption of Cadmium in artificial serum matrix:

The effects of some additives such as releasing agents on the absorption signal of Cadmium in artificial serum matrix are investigated and compared with that of standard solution at different temperatures. Results obtained at room temperature are shown in figure (3.38). As can be seen from the figure below that artificial serum matrix reduces the absorption signal of Cadmium, and more reduction in signal is obtained in case of adding EDTA as releasing agent, addition of ethanol (4) and citric acid addition.

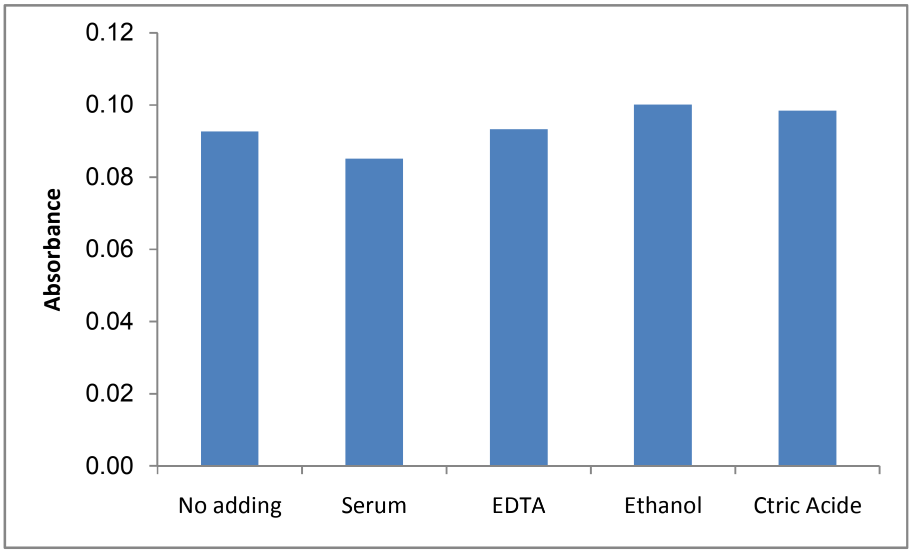

Figure (3.38): The absorbance of 0.5 ppm Cd in artificial serum solution with different additives at room temperature.

Figures (3.39 and 3.40) below show the effect of addition of some releasing agents to 0.5 ppm cadmium solution in presence of artificial serum solution at 50 and 80°C. From the figures below, better enhancement for absorption signal in all cases at higher temperatures, with ethanol the signal becomes even better than that for the standard solution.

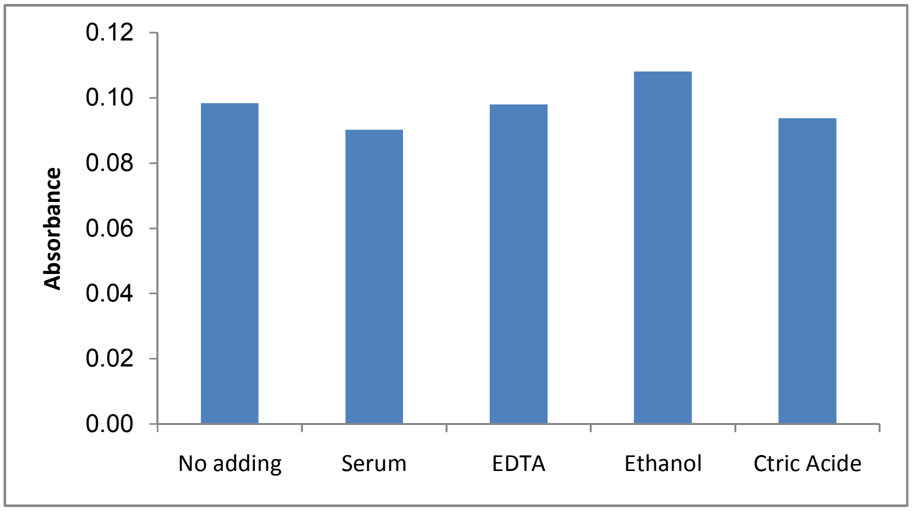

Figure (3.39): The absorbance of 0.5 ppm Cd in artificial serum solution with different additives at 50^0 C.

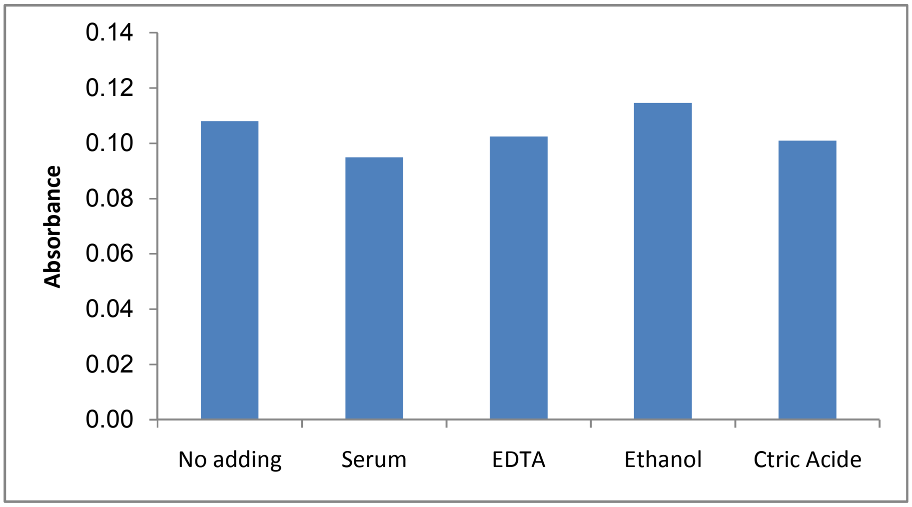

Figure (3.40): The absorbance of 0.5 ppm Cd in artificial serum solution with different additives at 80^0C.

3.4.3 Optimization of nickel analysis in presence of artificial serum solution:

Optimization of nickel analysis in presence of artificial serum matrix is investigated using 1 ppm Ni in artificial serum solution , the results obtained for fuel-oxidant Stoichiometry and burner height are shown in figures (3.41 a and 3.41 b) respectively. Better absorption values are obtained at 70 fuel oxidant and 10 mm burner height instead of 40 and 9 mm for standard solution.

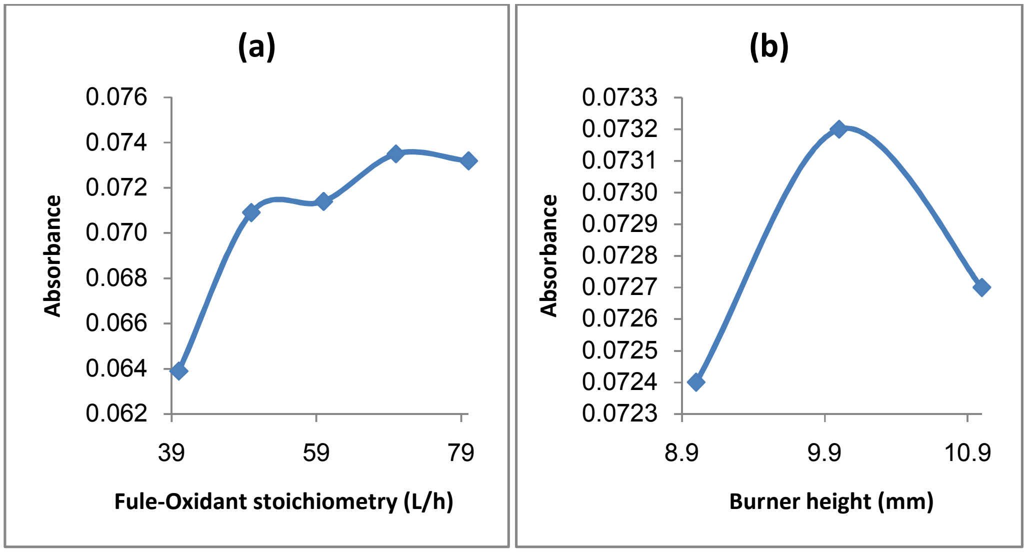

Figure (3.41): The effect of two parameters on absorbance signal of nickel analysis presence in artificial serum solution (a): effect of fuel-oxidant stoichiometry at burner height 10 (b): effect of burner height at 70 fuel-oxidant stoichiometry.

3.4.4 Effect of some additives on absorption of Nickel in artificial serum matrix:

The effects of some additives such as releasing agents on the absorption signal of Nickel in artificial serum matrix are investigated and compared with that of standard solution at different temperatures. Results obtained at room temperature are shown in figure (3.42). As can be seen from the figure below that artificial serum matrix reduces the absorption signal of Nickel**,** addition of EDTA and ethanol the signal becomes even better than that for the artificial serum solution, and with citric acid addition reduces the absorption signal of Nickel like artificial serum solution.

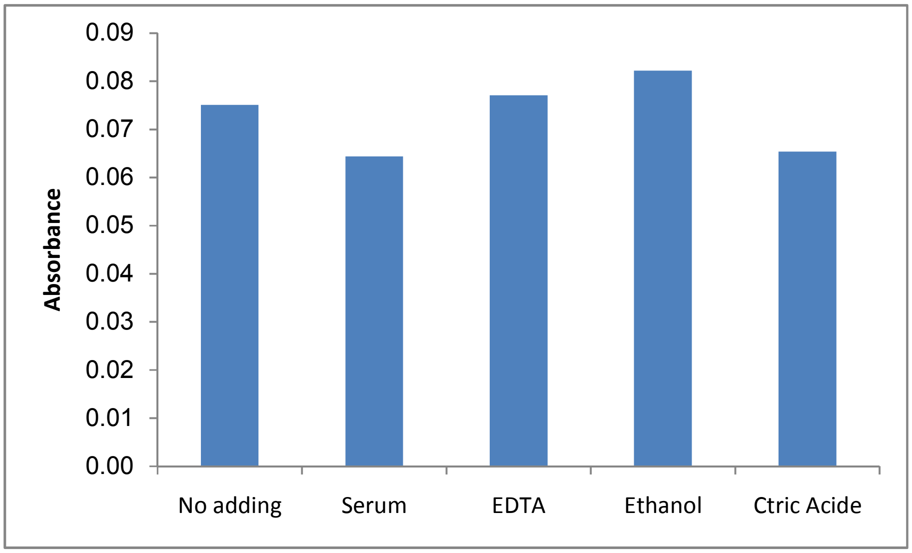

Figure (3.42): Absorbance of 1 ppm Ni in artificial serum solution with different additives at room temperature.

Figures (3.43 and 3.44) below show the effect of addition of some releasing agents to 1 ppm nickel solution in presence of artificial serum solution at 50 and 80 ^{0} C. From the figures below, better enhancement for absorption signal in all cases at higher temperatures, with ethanol and EDTA the signal becomes even better than that for the artificial serum solution.

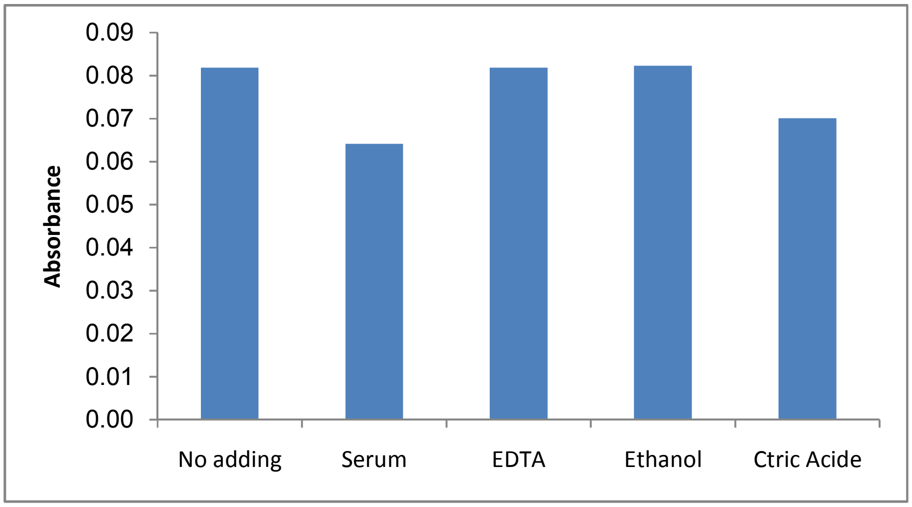

Figure (3.43): Absorbance of 1 ppm Ni in artificial serum solution with different additives at 50^{0}C.

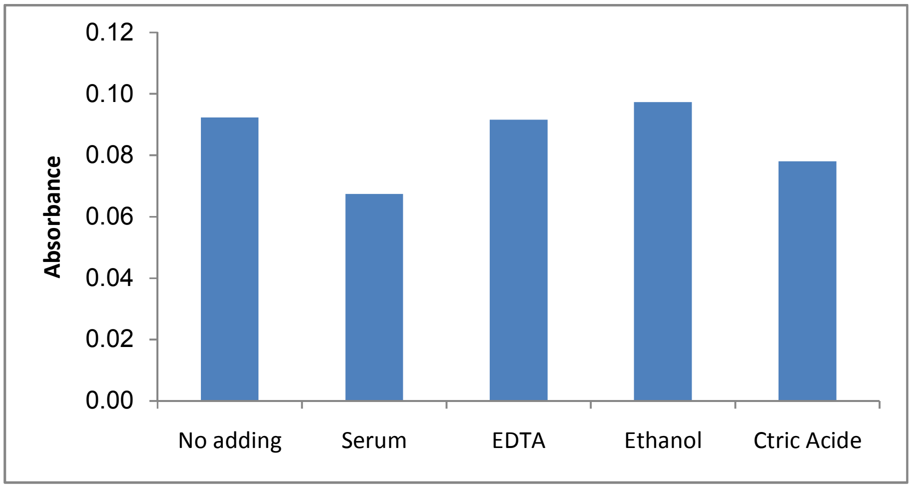

Figure (3.44): Absorbance of 1 ppm Ni in artificial serum solution with different additives at 80^{0}C.

3.4.5 Optimization of Chromium analysis in presence of artificial serum solution:

Optimization of Chromium analysis in presence of artificial serum matrix is investigated using 1.5 ppm Cr in artificial serum solution , the results obtained for fuel-oxidant Stoichiometry and burner height are shown in figures (3.45 a and 3.45 b) respectively. Better absorption values are obtained at 80 fuel oxidant and 10 mm burner height instead of 100 and 10 mm for Chromium in case of standard solution.

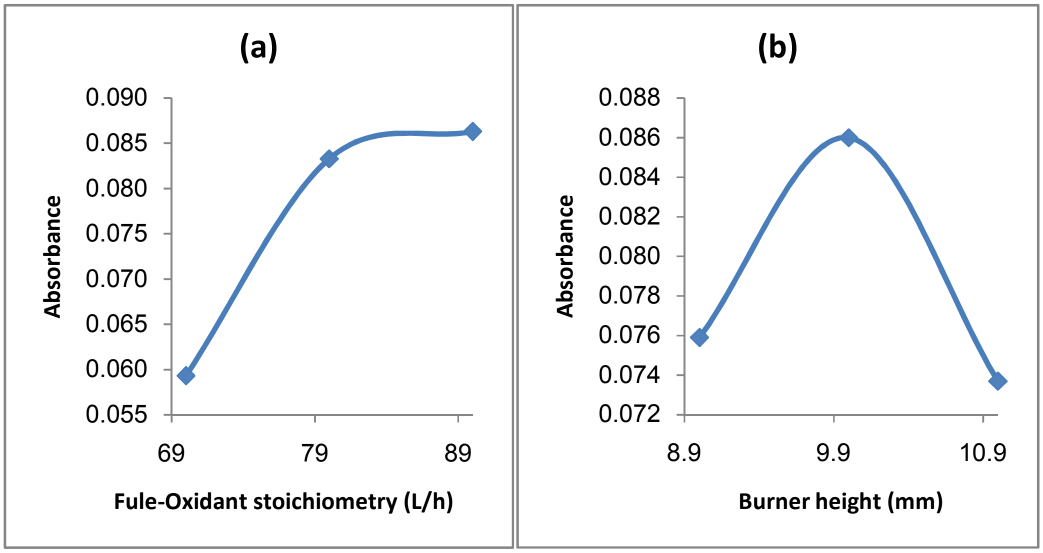

Figure (3.45): The effect of two parameters on absorbance signal of chromium analysis presence in artificial serum solution (a): effect of fuel-oxidant stoichiometry at burner height 11 (b): effect of burner height at 80 fuel-oxidant stoichiometry.

3.4.6 Effect of some additives on absorption of Chromium in artificial serum matrix:

The effects of some additives such as releasing agents on the absorption signal of Chromium in artificial serum matrix are investigated and compared with that of standard solution at different temperatures. Results obtained at room temperature are shown in figure (3.46). As can be seen from the figure below, that artificial serum matrix reduces the absorption signal of Chromium, and increasing in signal is obtained in case of adding EDTA as releasing agent, addition of ethanol and citric acid addition works much better than EDTA in presence of serum matrix.

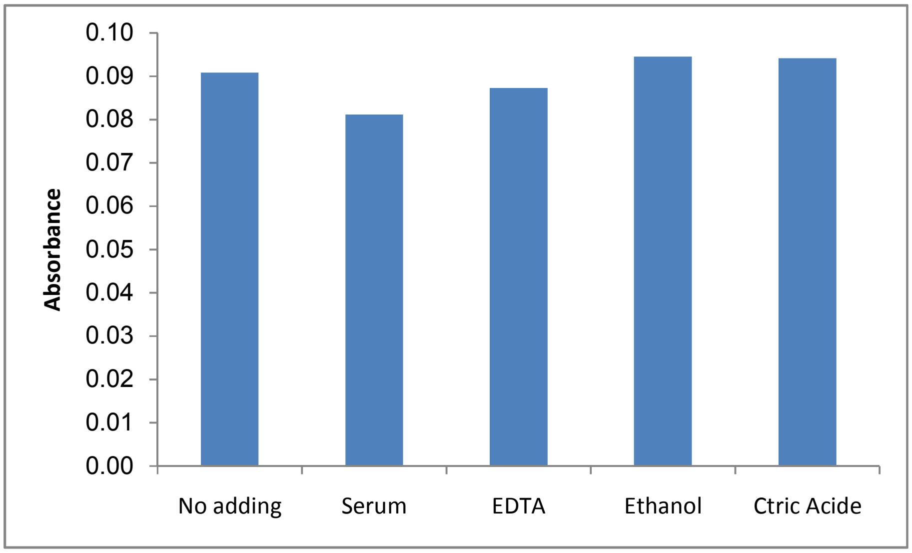

Figure (3.46): Absorbance of 1.5 ppm Cr in artificial serum solution with different additives at room temperature.

Figures (3.47 and 3.48) below shows the effect of addition of some releasing agents to 1.5 ppm Chromium solution in presence of artificial serum solution at 50 and 80^{0}C. From the figures below, better enhancement for absorption signal in all cases at higher temperatures, with Citric acid the signal becomes even better than that for the standard solution.

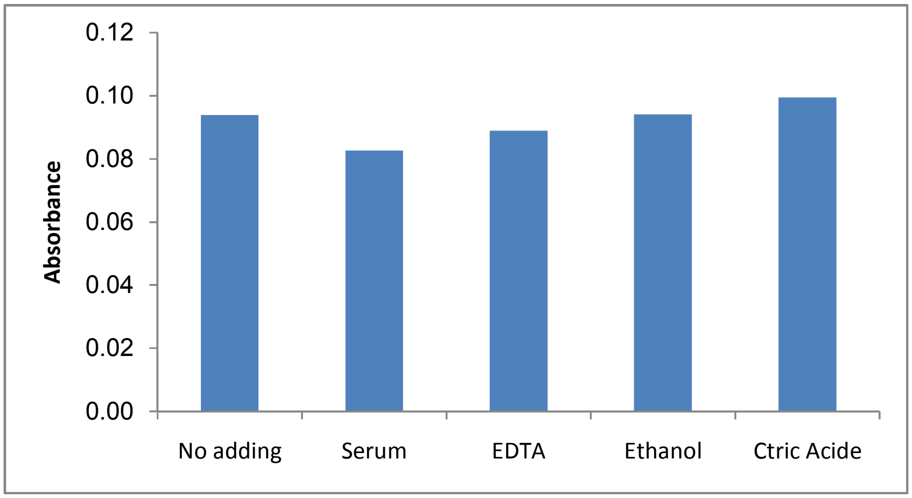

Figure (3.47): Absorbance of 1.5 ppm Cr in artificial serum solution with different additives at 50^{0}C.

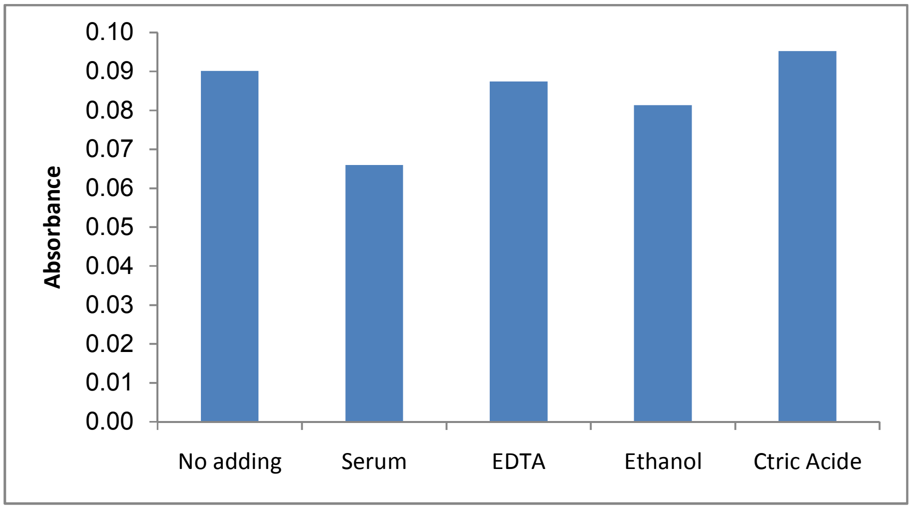

Figure (3.48): Absorbance of 1.5 ppm Cr in artificial serum solution with different additives at 80^{0}.

3.4.7 Optimization of Manganese analysis in presence of artificial serum solution:

Optimization of Manganese analysis in presence of artificial serum matrix is investigated using 1 ppm Mn in artificial serum solution , the results obtained for fuel-oxidant Stoichiometry and burner height are shown in figures (3.49.a and 3.49.b) respectively. Better absorption values are obtained at 65 fuel oxidant and 10 mm burner height instead of 60 and 9 mm for standard solution.

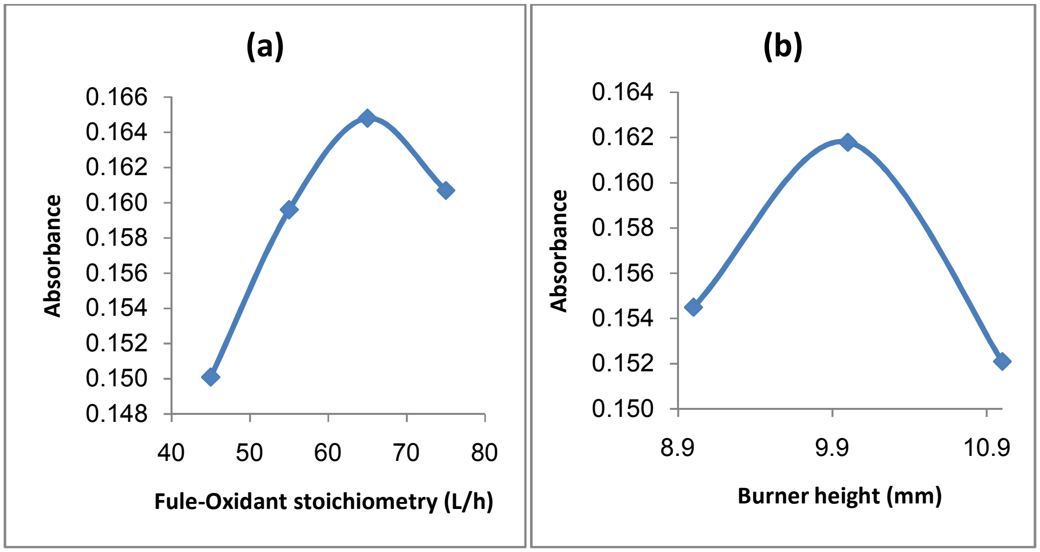

Figure (3.49): The effect of two parameters on absorbance signal of manganese analysis presence in artificial serum solution (a): effect of fuel-oxidant stoichiometry at burner height 10 (b): effect of burner height at 65 fuel-oxidant stoichiometry.

3.4.8 Effect of some additives on absorption of Manganese in artificial serum matrix:

The effects of some additives such as releasing agents on the absorption signal of Manganese in artificial serum matrix are investigated and compared with that of standard solution at different temperatures. Results obtained at room temperature are shown in figure (3.50). As can be seen from the figure below, that artificial serum matrix reduces the absorption signal of Manganese, and better signal is obtained in case of adding EDTA as releasing agent, addition of ethanol and citric acid addition show better absorption signal than that for EDTA and matrix alone.

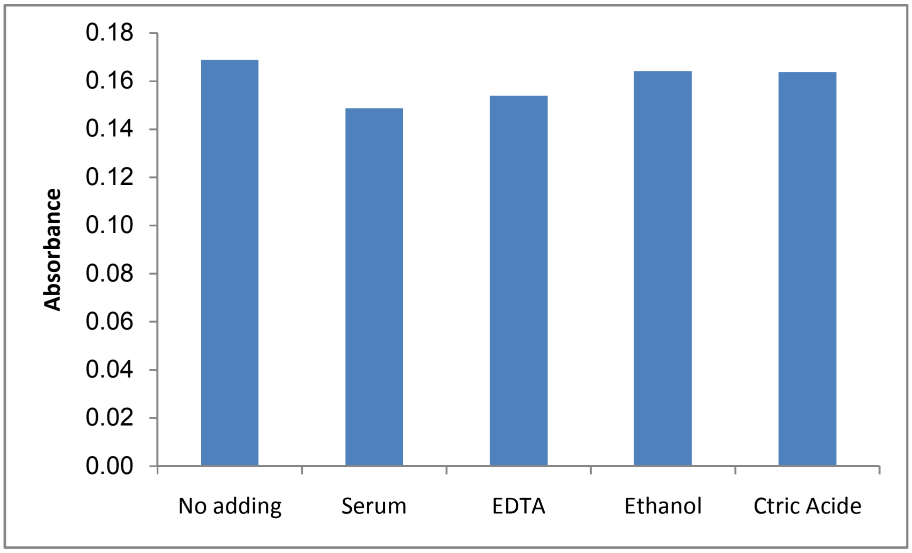

Figure (3.50): Absorbance of 1 ppm Mn in artificial serum solution with different additives at in at room temperature.

Figures (3.51) and (3.52) below show the effect of addition of some releasing agents to 1.5 ppm Manganese solution in presence of artificial serum solution at 50 and 80^{0}C. From the figures below, better enhancement for absorption signal in all cases at higher temperatures.

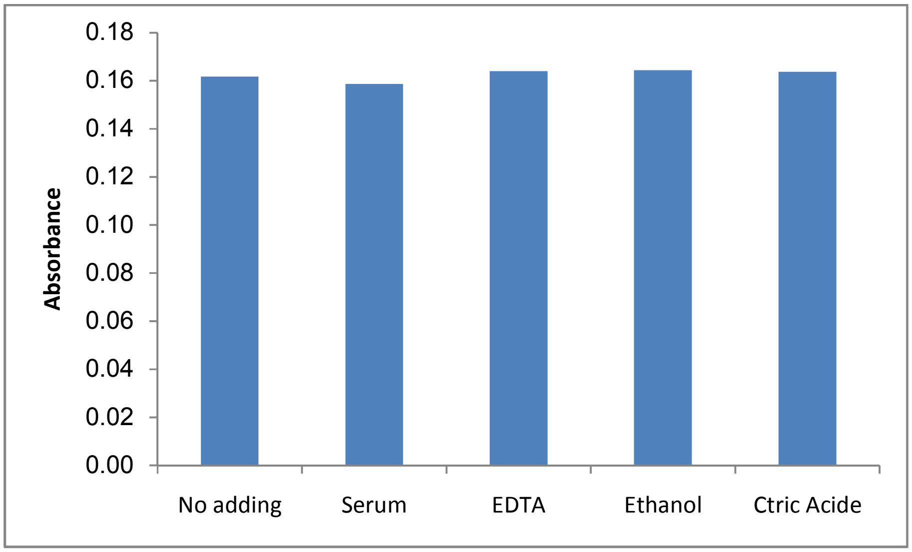

Figure (3.51): Absorbance of 1 ppm Mn in artificial serum solution with different additives at in at 50^{0}C.

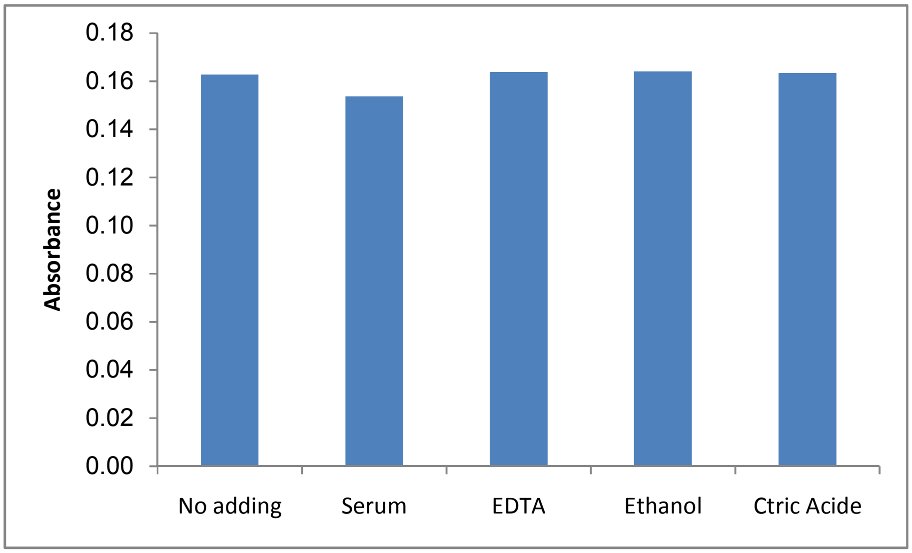

Figure (3.52): Absorbance of 1 ppm Mn in artificial serum solution with different additives at in at 80^{0}C.

3.5 Summary of the results:

Table (3.1): Optimization of chromium analysis in standard solution and different matrices.

Optimization of 2 ppm standard solution	Fuel-oxidant stoichiometry	Flame height	Absorbance
	100	10	0.0866
Optimization of 2 ppm standard solution in 5% NaCl solution	Fuel-oxidant stoichiometry	Flame height	Absorbance
	80	9	0.0865
Optimization of 1.5 ppm standard solution in artificial urine solution	Fuel-oxidant stoichiometry	Flame height	Absorbance
	90	11	0.0508
Optimization of 1.5 ppm standard solution in artificial serum solution	Fuel-oxidant stoichiometry	Flame height	Absorbance
	80	10	0.0860

Table (3.2): Optimization of nickel analysis in standard solution and different matrices.

Optimization of 2 ppm standard solution	Fuel-oxidant stoichiometry	Flame height	Absorbance
	50	9	0.1307
Optimization of 2 ppm standard solution in 5% NaCl	Fuel-oxidant stoichiometry	Flame height	Absorbance
	60	8	0.1425
Optimization of 1.5 ppm standard solution in artificial urine	Fuel-oxidant stoichiometry	Flame height	Absorbance
	50	10	0.0521
Optimization of 1.5 ppm standard solution in artificial serum	Fuel-oxidant stoichiometry	Flame height	Absorbance
	70	10	0.0735

SD= 0.001958 ± 0.0000766; n= 4 with pre-suction.

Table (3.3): Optimization of manganese analysis in standard solution and different matrices.

Optimization of 2 ppm standard solution	Fuel-oxidant stoichiometry	Flame height	Absorbance
	60	9	0.1905
Optimization of 2 ppm standard solution in 5% NaCl	Fuel-oxidant stoichiometry	Flame height	Absorbance
	65	10	0.2602
Optimization of 1.5 ppm standard solution in artificial urine	Fuel-oxidant stoichiometry	Flame height	Absorbance
	55	12	0.1329
Optimization of 1.5 ppm standard solution in artificial serum	Fuel-oxidant stoichiometry	Flame height	Absorbance
	65	10	0.1618

Table (3.4): Optimization of cadmium analysis in standard solution and different matrices.

Optimization of 2 ppm standard	Fuel-oxidant stoichiometry	Flame height	Absorbance
	40	9	0.3113
Optimization of 2 ppm standard solution in 5% NaCl	Fuel-oxidant stoichiometry	Flame height	Absorbance
	40	7	0.3367
Optimization of 1.5 ppm standard solution in artificial urine	Fuel-oxidant stoichiometry	Flame height	Absorbance
	40	7	0.3353
Optimization of 1.5 ppm standard solution in artificial serum	Fuel-oxidant stoichiometry	Flame height	Absorbance
	40	7	0.1014

SD= 0.001958 ± 0.0000766; n= 4 with pre-suction.

Table (3.5): Effect of additive agents on chromium analysis in different matrices.

	Additive agents effect on 2 ppm standard solution in 5% NaCl	1	2	3	4	5
Different temperatures	Room temp.	0.0759	0.0719	0.0752	0.0899	0.0932
	50	0.0769	0.0701	0.0548	0.0718	0.0956
	80	0.0917	0.0700	0.0467	0.0724	0.0953
	Additive agents effect on 1.5 ppm standard solution in artificial urine	1	2	3	4	5
Different temperatures	Room temp.	0.0802	0.0556	0.0889	0.0791	
	50	0.0796	0.0581	0.0906	0.0795	
	80	0.0811	0.0563	0.0976	0.0688	
	Additive agents effect on 1.5 ppm standard solution in artificial serum	1	2	3	4	5
Different temperatures	Room temp.	0.0908	0.0812	0.0873	0.0945	0.0942
	50	0.0939	0.0826	0.0889	0.0941	0.0995
	80	0.0901	0.0660	0.0874	0.0814	0.0952

1 is metal ion in standard Solution , 2 is metal ion in matrix solution , 3 is metal ion in matrix solution with adding EDTA at desired P^H , 4 is metal ion in matrix solution with adding ethanol , 5 is metal ion in matrix solution with adding citric acid.

SD= 0.001958 ± 0.0000766; n= 4 with pre-suction.

Table (3.6): Effect of additive agents on nickel analysis in different matrices.

	Additive agents effect on 2 ppm standard solution in 5% NaCl	1	2	3	4	5
Different temperatures	Room temp.	0.1469	0.1401	0.1353	0.1451	0.1339
	50	0.1530	0.1476	0.1475	0.1657	0.1401
	80	0.1576	0.1482	0.1454	0.1651	0.1450
	Additive agents effect on 1.5 ppm standard solution in artificial urine	1	2	3	4	5
Different temperatures	Room temp.	0.0878	0.0799	0.0731	0.0858	
	50	0.0918	0.0816	0.0818	0.0960	
	80	0.0903	0.0815	0.0842	0.0995	
	Additive agents effect on 1.5 ppm standard solution in artificial serum	1	2	3	4	5
Different temperatures	Room temp.	0.0751	0.0644	0.0771	0.0822	0.0654
	50	0.0819	0.0641	0.0819	0.0823	0.0701
	80	0.0923	0.0674	0.0916	0.0973	0.0781

1 is metal ion in standard Solution , 2 is metal ion in matrix solution , 3 is metal ion in matrix solution with adding EDTA at desired P^H , 4 is metal ion in matrix solution with adding ethanol , 5 is metal ion in matrix solution with adding citric acid.

SD= 0.001958 ± 0.0000766; n= 4 with pre-suction.

Table (3.7): Effect of additive agents on manganese analysis in different matrices.

	Additive agents effect on 2 ppm standard solution in 5% NaCl	1	2	3	4	5
Different temperatures	Room temp.	0.3001	0.2625	0.2488	0.2511	0.2515
	50	0.3027	0.2617	0.2479	0.2646	0.2540
	80	0.3195	0.2684	0.2629	0.2674	0.2576
	Additive agents effect on 1.5 ppm standard solution in artificial urine	1	2	3	4	5
Different temperatures	Room temp.	0.1306	0.1246	0.1159	0.1329	
	50	0.1435	0.1289	0.1143	0.1377	
	80	0.1474	0.1119	0.1106	0.1326	
	Additive agents effect on 1.5 ppm standard solution in artificial serum	1	2	3	4	5
Different temperatures	Room temp.	0.1689	0.1488	0.1539	0.1641	0.1638
	50	0.1617	0.1588	0.1640	0.1644	0.1638
	80	0.1628	0.1538	0.1639	0.1641	0.1634

1 is metal ion in standard Solution , 2 is metal ion in matrix solution , 3 is metal ion in matrix solution with adding EDTA at desired PH , 4 is metal ion in matrix solution with adding ethanol , 5 is metal ion in matrix solution with adding citric acid.

SD= 0.001958 ± 0.0000766; n= 4 with pre-suction.

Table (3.8): Effect of additive agents on cadmium analysis in different matrices.

	Additive agents effect on 2 ppm standard solution in 5% NaCl	1	2	3	4	5
Different temperatures	Room temp.	0.3572	0.3287	0.3305	0.3457	0.3232
	50	0.3363	0.314	0.3316	0.3472	0.2985
	80	0.3183	0.3011	0.3080	0.3605	0.3117
	Additive agents effect on 1.5 ppm standard solution in artificial urine	1	2	3	4	5
Different temperatures	Room temp.	0.0941	0.0701	0.0936	0.0946	
	50	0.1075	0.0790	0.1052	0.1169	
	80	0.1023	0.0840	0.1070	0.1251	
	Additive agents effect on 1.5 ppm standard solution in artificial serum	1	2	3	4	5
Different temperatures	Room temp.	0.0927	0.0852	0.0933	0.1001	0.0984
	50	0.0984	0.0902	0.098	0.1081	0.0938
	80	0.108	0.095	0.1025	0.1147	0.1009

1 is metal ion in standard Solution , 2 is metal ion in matrix solution , 3 is metal ion in matrix solution with adding EDTA at desired P^H , 4 is metal ion in matrix solution with adding ethanol , 5 is metal ion in matrix solution with adding citric acid.

SD= 0.001958 ± 0.0000766; n= 4 with pre-suction.

As can be seen from above tables the values of fuel-oxidant, burner height and hence absorbance is varied for metal ions in standard solution and for that in presence of sodium chloride, urine and serum.

For example 2 ppm Cr signal was 0.0866 in standard solution with 100 l/h fuel-oxidant and 10 mm for burner height, increasing of pretreatment temperature reduces the absorption signal, and this may be attributed to the increase of absorption of chromium on the glass wall of the container or precipitation of chromium.

In case of artificial urine, the absorption signal reduced up to 40% of that for standard solution and enhancement of signal were achieved by addition of ethanol and EDTA.

For nickel in sodium chloride no effect on signal was detected this means that we can measure nickel in sodium chloride at higher concentration (sea water for example) freely from interferences of the clear effect on absorption signal in case of urine and serum but enhancement could be reached up to about 35% by addition of EDTA and ethanol.

Different behavior could be seen for manganese and cadmium in presence of different matrices as shown in tables above.

4. Conclusion:

The critical instrumental parameters such as burner height and fuel-oxidant stoichiometry are not always the same for analyzing metal ions in standard solution and in presence of different matrices.

Addition of releasing agents such as EDTA and additives such as ethanol and citric acid during analysis of metal ions in presence highly interfering matrices reduces the interferences.

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جامعة بنغازى

كلية العلوم

قسم الكيمياء

"ايجاد القيم المثلى للمتغيرات الالية الحرجة في تحليل بعض المعادن الضئيلة فى عينات مختلفة بواسطة المطياف اللهبي "

لاكمال متطلبات الحصول على درجة الاجازة العليا فى العلوم-الكيمياء
(الماجستير)

مقدم من الطالب :
عطية سليمان على سمور

تحت اشراف :
أ. د. عوض عبد الحميد الحصادى
د. عبد السلام على اسويسي

بنغازى - ليبيا

2013- 2014

الملخص

المتغيرات الالية الحرجة لها تأثير ملحوظ خلال تحليل العناصر ضئيلة الكمية باستخدام طريقة المطياف اللهبي .

ارتفاع اللهب ونسبة اتزان الوقود و العامل الموكسد اختبرت لقياس النيكل , المغنسيوم , الكروم و الكادميوم فى المحاليل القياسية وفى العينات ذات التداخلات العالية مثل 5% كلوريد الصوديوم , مصل الدم , البول .

واختبرت اضافة بعض العوامل المحررة (Releasing Agents) وبعض الاضافات (Additive Agents) مثل EDTA و الايثانول وحمض الستريك لعينات التحليل لكى تقلل خلفية الاشارة وتحفز الحساسية والتكرارية للقياسات .

و اختبرت تلك الاضافات عند درجات حرارة مختلفة (درجة حرارة الغرفة , 50 مئوى , 80 مئوى).