Chapter (3) Results and Discussion

3.1. Determination of chromium by atomic absorption technique

The use of atomic absorption spectroscopy in our laboratories for the determination of chromium element in geological matrices of good accuracy and precision is required. Calibration and optimization of the instrument that led to high efficiency in the determination of chromium with acceptable detection limit. It is included the best determination of λ_{max} at maximum absorption and the suitable method for opening the rock and mineral samples.

The instrumental conditions (flame composition, and the observation height) was examined and optimized. The effects of different concentration of mineral acids on the sensitivity of Cr absorption were studied. Also, the effects of foreign ions that present in the matrix solution on the absorbance of chromium

were evaluated. This investigation was certified by application on some reference standard rocks.

3.1.1. Optimization of parameters by atomic absorption technique

The parameters which affect accuracy, precision, and sensitivity are burner height and fuel flow.

3.1.1.1. Flame composition

Beside the qualitative nature of the gas mixture, the quantitative mixing ratio is very important for characterizing the flame. Thus, it was possible to distinguish between sooting flames (only with organic fuels), fuel rich flames, stoichiometric flames, and fuel lean flames which depend on the fuel-oxygen ratio. Fuel rich flames were proved to be good for determining metals that have a strong tendency to form oxides. The oxide formation in general is not significant with alkalis, but alkali hydroxides are frequently formed in fuel-lean flames

The fuel flow rate is often very critical in the air-acetylene flames. Some of the elements show complex flow rate. The plots of the flow rate versus absorbance show that the least rate of change of absorbance is at the stoichiometric flow rate. Careful adjustment of the acetylene flow rate can minimize the interference expected by other elements present in the matrix. On the other hand, a very slight increase in flow rate occurs in a considerable difference in the absorbances. And due to the critical effect of the acetylene flow rate on the relative absorbance, matrix matching of sample and calibration solutions is very important in the air-acetylene flame. The optimization of the acetylene flow rate is also necessary for this flame to achieve the maximum sensitivity.

The influence of the flame composition on the absorption signal value at concentration level of 3 μg/mL of chromium at λ_{max} 359.7 nm was studied. The relation between the acetylene flow rate and the intensity of chromium absorbance is represented in Table (1) and illustrated in Fig. (1). It showed that the optimum acetylene flow rate was 2.4 L/ min.

3.1.1.2. Observation height

It is useful to know the burner height setting at which the burner cuts into the light path. This can be simply done by initially auto zeroing and then raising the burner towards the line path (i.e. towards zero on the burner height indicator) and noting the height at which the digital display starts to increase. The effect of change of observation height on the absorption signal intensity of 3 μg/mL chromium at λ_{max} 359.7 nm was investigated. The obtained data are given in Table (2) and illustrated in Fig. (2). It is confirmed that the change in the height of observation has a marked effect on the analyte absorption. The highest signal value observed at 10.98 mm burner height.

Table (1): Effect of acetylene flow rate on 3 µg/mL Cr absorbance

Acetylene flow rate, L/min	Absorbance
1.4	0.005
1.6	0.017
1.8	0.040
2.0	0.075
2.2	0.132
2.4	0.199
2.8	0.153

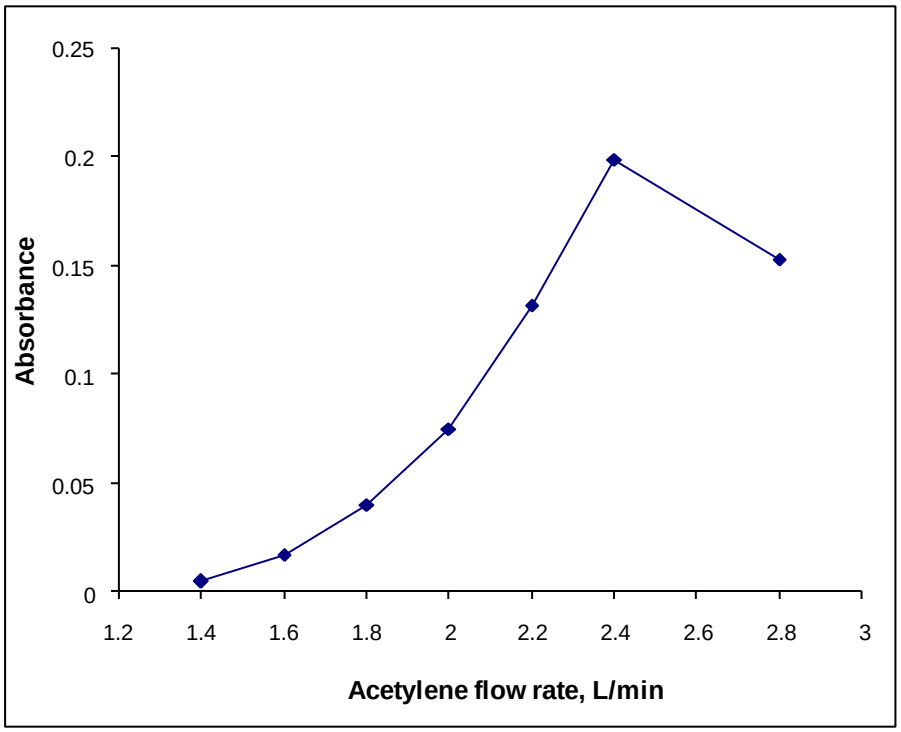

Figure (1): Effect of acetylene flow rate on 3 µg/mL Cr absorbance

Table (2): Effect of burner height on the absorbance of 3 μg/mL Cr

Burner height, mm	**Absorbance**
2.98	0.106
3.78	0.086
4.58	0.072
5.38	0.067
6.18	0.075
6.98	0.098
7.78	0.125
8.58	0.153
9.38	0.176
10.18	0.191
10.98	0.201
11.78	0.200
12.58	0.197
13.38	0.188
14.18	0 .179

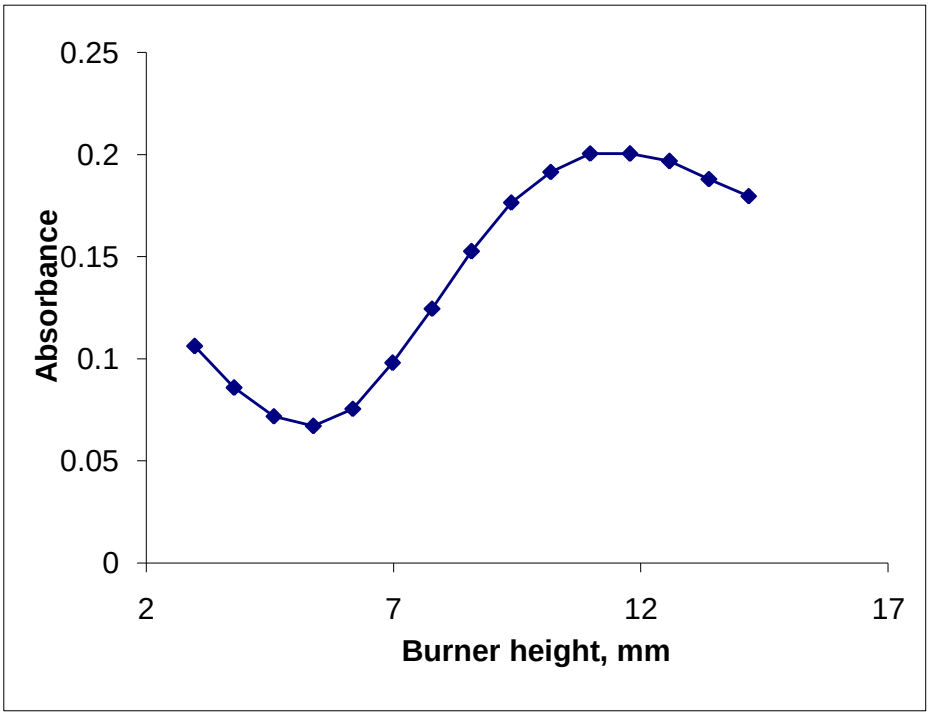

Figure (2): Effect of burner height on the absorbance of 3 µg/mL Cr

3.1.1.3. Repeatability

Repeatability means the precision obtained with an analytical method in one particular occasion, using the same equipment and the same solutions. The repeatability of 3 µg/mL of chromium and blank were determined by running six replicated samples at λ_{max} 359.7 nm. Furthermore, the standard deviation of the samples

was 0.001 and 0.0005, respectively. The results obtained were shown in Table (3 and 4).

3.1.1.4. Calibration curve

Calibration curve was carried out for chromium at 10.98 mm burner height and 2.4 L/ min acetylene flow rate at λ_{max} 359.7 nm. Table (5) illustrates the data obtained by atomic absorption method for chromium under investigation. Beer's law was verified and found to be satisfactory obeyed for the concentration range 0.5– 6 µg/ml for chromium. This is shown in Fig. (3).

Table (3): Repeatability of 3 µg/mL Cr

Resample No	Absorbance
1	0.198
2	0.197
3	0.198
4	0.199
5	0.199
6	0.200
Mean	0.199
SD	0.001
RSD%	0.500

Table (4): Repeatability of blank

Resample No	Absorbance
1	0.00
2	0.00
3	0.00
4	0.00
5	0.00
6	0.00
Mean	0.0003
SD	0.0005

Table (5): Data of Calibration curve of chromium using fuel rich air acetylene

Cr, µg/ml	Absorbance
0.5	0.036
1	0.070
2	0.132
3	0.198
4	0.250
5	0.300
6	0.380

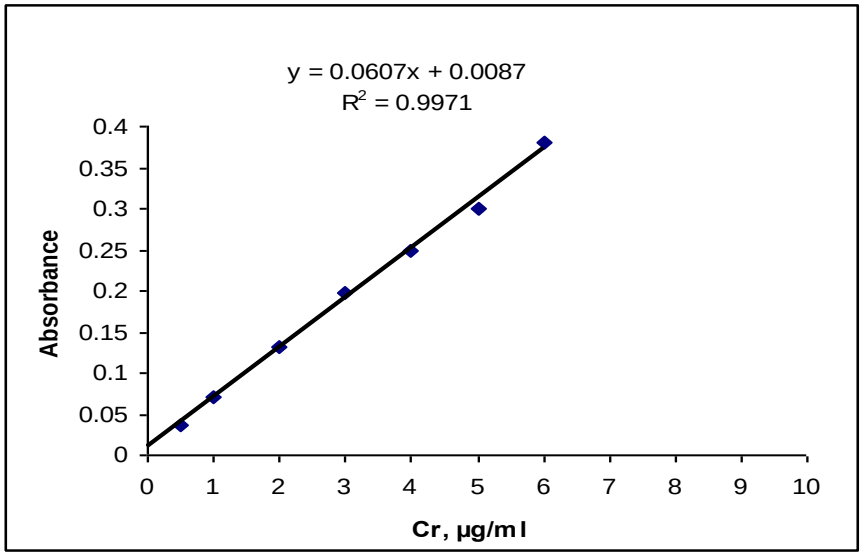

Figure (3): Calibration curve of chromium using fuel rich air acetylene

3.1.2. Interferences studies

Chromium assaying rock of mineral solutions by atomic absorption technique is rended difficult by the fact that diverse ions interfere in the determination with varying degree of success to suppress interferences.

3.1.2.1. Effect of diverse ions

1000 μg/mL from Ca^{+2}, Mg^{+2}, Mn^{+2}, Ba^{+2}, Fe^{+3}, Co^{+2}, Cu^{+2}, Ni^{+2} and Al^{+3} was added one by one to 3 μg/ml of chromium and the absorbance was measured. The results obtained are given in Table (6). Evidently, barium and manganese elements had no influence on the absorbance of chromium. These diverse ions do not interfere in the determination of chromium over the ranges investigated in this work. On the other side, Ca^{+2}, Mg^{+2}, Al^{+3}, Ni^{+2}, Fe^{+3}, Co^{+2}, Cu^{+2} ions cause depressive effect in the value of chromium absorbance.

The addition of 1% ammonium chloride [76] as a masking agent was showed no interference for Ca^{+2}, Mg^{+2}, and Ni^{+2} ions at

1000 μg/mL and for Al^{+3} ion at concentration of 500 μg/mL. However, the addition of 1% ammonium fluoride and 0.2% sodium sulphate were showed no interference of Co^{+2} and Fe^{+3} ions at 1000 μg/mL. On the other hand, 1% ammonium fluoride was showed no interference for Cu^{+2} ion at 1000 μg/mL. This was detected in Table (6).

Table (6): Tolerance limit of diverse ions on the determination of 3 μg/mL of chromium.

Foreign ion added	Tolerance limit (μg/ml)
[a] Ca^{+2}	1000
Ba^{+2}	1000
[a] Mg^{+2}	1000
Mn^{+2}	1000
[b] Co^{+2}	1000
[a] Ni^{+2}	1000
[c] Cu^{+2}	1000
[a] Al^{+3}	500
[b] Fe^{+3}	1000

[a] 1% ammonium chloride
[b] 1% ammonium chloride+ 0.2% sodium sulphate
[c] 1% ammonium fluoride

3.1.2.2. Effect of mineral acids

The effect of mineral acids concentrations (hydrochloric acid, nitric acid, sulfuric acid and phosphoric acid) used in an analytical procedure on 3 μg/mL chromium absorption signal was estimated at different molarities (0.25, 0.5, 1, 1.5, 2, and 2.5 M). A depressive effect was observed due to the presence of sulfuric and phosphoric acids solutions. The obtained results were shown in Table (7) and illustrated in Fig. (4). It was clearly shown that, nitric and hydrochloric acid had no effect on the absorption signal of chromium. On the other hand, the depressive effect of sulfuric and phosphoric acids might be attributed to the formation of less volatile (stable) compounds with analyte and these compounds are stable at the flame temperature.

Table (7): Effect of mineral acids concentrations on 3 µg/mL Cr absorbance

Conc. (M)	Absorbance			
	H_3PO_4	H_2SO_4	HCl	HNO_3
0.00	0.190	0.190	0.190	0.190
0.25	0.190	0.190	0.190	0.188
0.50	0.190	0.188	0.190	0.187
1.00	0.178	0.169	0.190	0.190
1.50	0.163	0.157	0.190	0.190
2.00	0.149	0.141	0.190	0.190
2.50	0.135	0.132	0.190	0.188

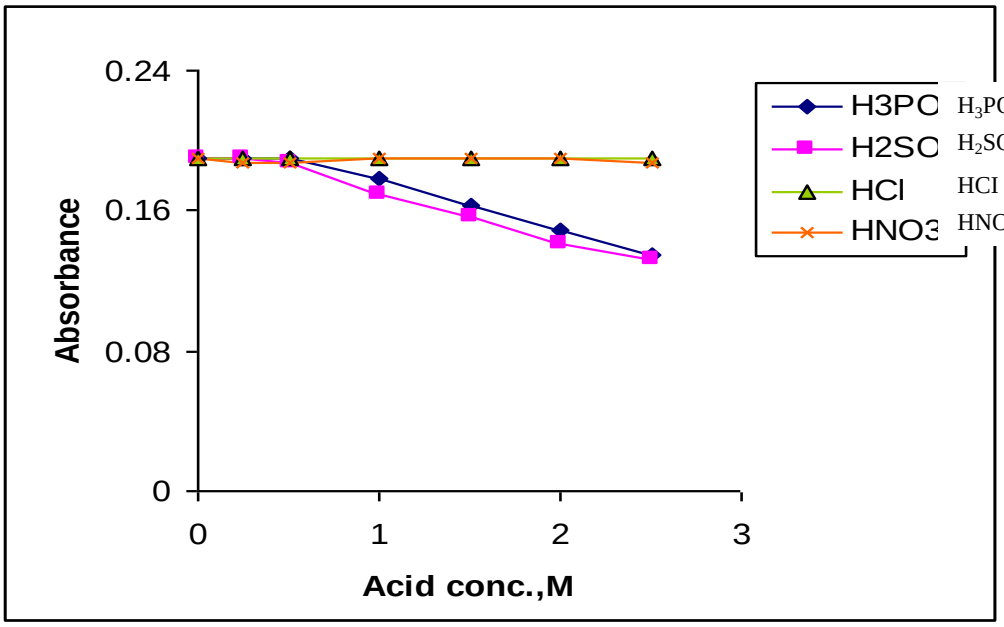

Figure (4): Effect of minerals acids concentrations on 3 µg/mL Cr absorbance

3.2. Spectrophotometric determination of chromium (VI) using thymol blue and dimethyl yellow reagents

3.2.1. The optimum reaction conditions for complex formation

3.2.1.1. Effect of pH

The most suitable pH values for the formation of chromium complexes with TB and DMY reagents were determined by scanning the absorption spectra of 1.0x 10^{-4} M solution of the metal complexes Fig.(5 and 6), within the wavelength range (300-700 nm) using the same amount of reagent at the same pH value as blank. The best pH for complex formation between Cr **(**VI**)** and TB and DMY reagents were 2.93 and 3.76 using acetate buffer solution which give best absorbance at λ_{max} 548 and 484 nm, respectively. The optimum pH curves were represented in Fig. (7) and it was detected in Table (8).

3.2.1.2. Effect of reagent concentration

To study the effect of reagent concentration on the complex formation, the concentration of metal ion was kept constant 1.0 x10^{-4} M, while that of the reagent was regularly

varied (1.0, 1.5……, 3.5 mL) of 1.0 $x10^{-3}$ M and the optimum volume of buffer for each complex was recorded in Table (9) and was shown in Fig. (8). The volume was completed with bidistilled water in case of TB reagent and with ethanol in case of DMY reagent to the mark of 10 mL measuring flask. The absorption spectrum was recorded against blank solution prepared in the same manner without the metal ion. The absorbance was plotted against mL added of reagents as shown in Fig. (9). The optimum concentration of reagent was recorded in Table (10). We found that, the optimum reagent concentration for Cr **(**VI**)** was 3.0 mL of $1.0x10^{-3}$ M of TB and DMY reagents.

3.2.1.3. Effect of sequence of addition

The results of different sequences of addition to select the most suitable one for developing the concerned complexes was investigated by measuring the absorbance of solutions prepared by different sequence of addition in the visible region against a blank solution prepared in the same manner. Experiments showed that the order "Metal- Buffer- Reagent" gave the best results for

complex between TB and Cr **(**VI**)** and "Metal- Reagent -Buffer" for complex between DMY and Cr **(**VI**)**. This was detected in Table (11) and was shown in Fig. (10).

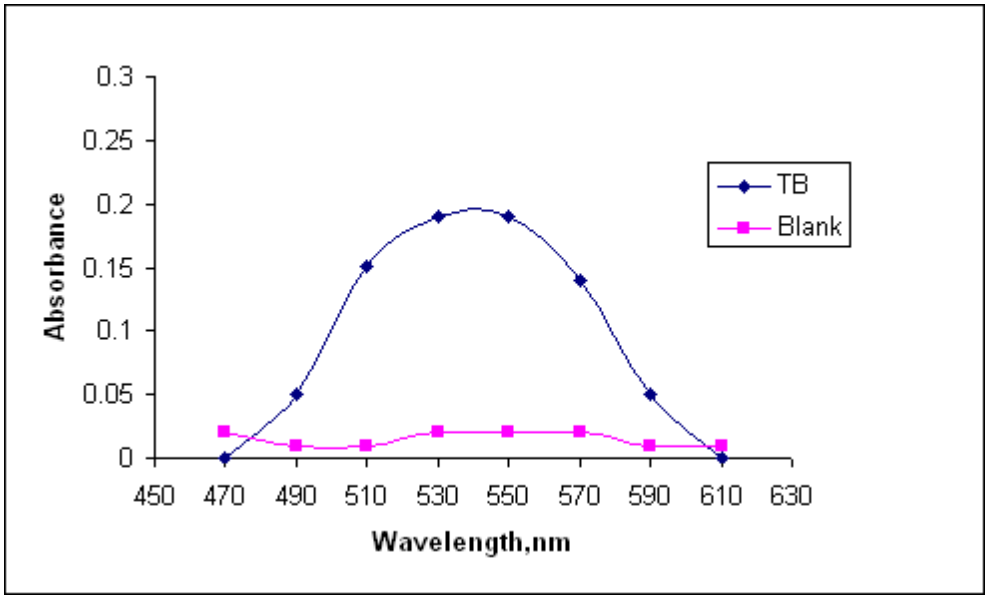

Figure (5): Absorption spectra of colored chromium complex using TB reagent.

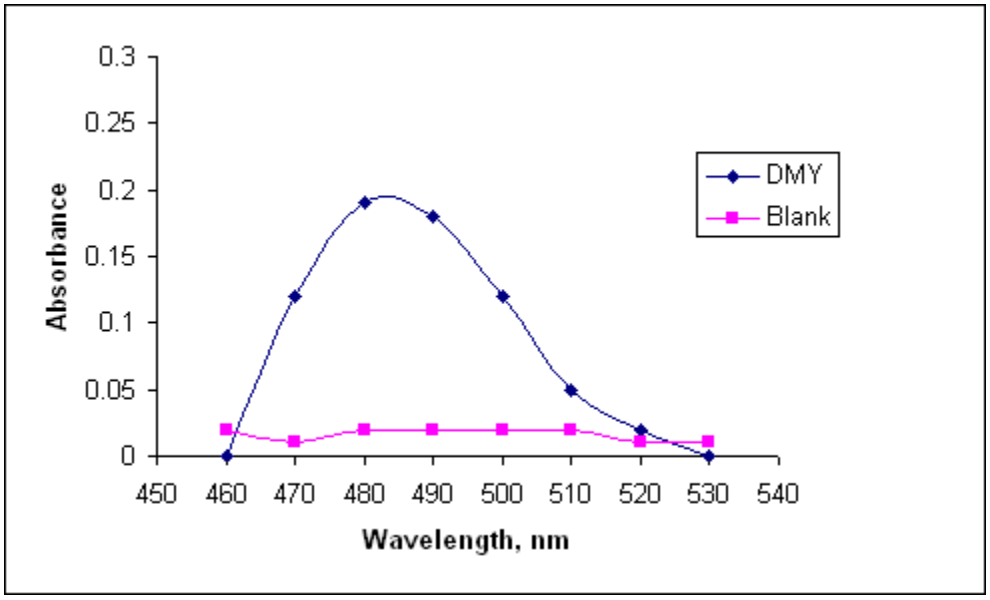

Figure (6): Absorption spectra of colored chromium complex using DMY reagent.

Table (8): Effect of pH on the absorbance of chromium **(**VI) using TB and DMY reagents.

pH	Absorbance	
	Thymol blue	**Dimethyl yellow**
1.75	0.050	0.090
2.13	0.110	0.140
2.93	0.194	0.180
3.76	0.015	0.190
4.71	0.002	0.163
5.82	0.001	0.162

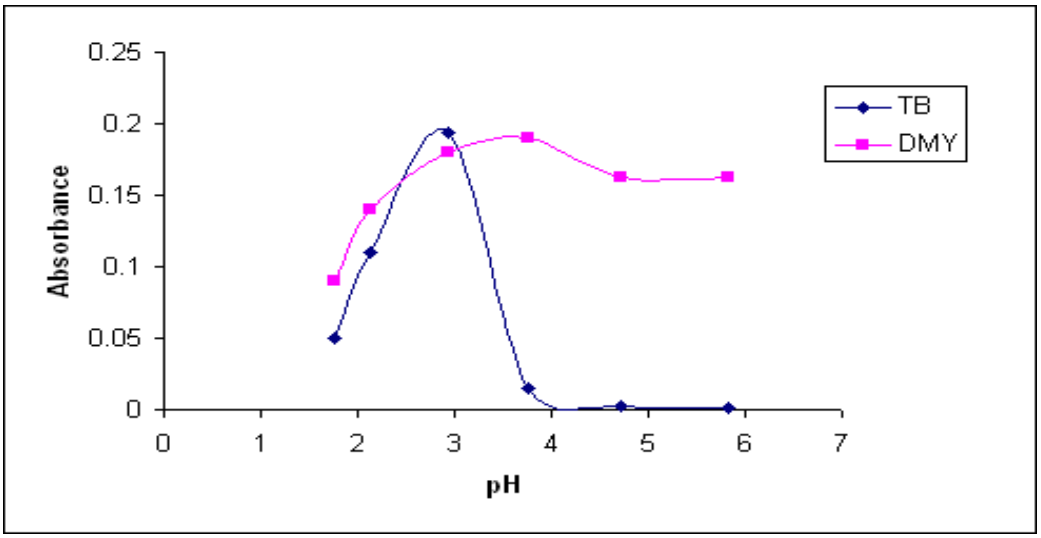

Figure (7): Effect of pH on the absorbance of chromium **(**VI) using TB and DMY reagents

Table (9): Effect of volume of buffer on the absorbance of chromium **(**VI) using TB and DMY reagents.

Buffer volume, mL	**Absorbance**	
	Thymol blue	**Dimethyl yellow**
1	0.266	0.204
2	0.218	0.177
3	0.194	0.163
4	0.191	0.161

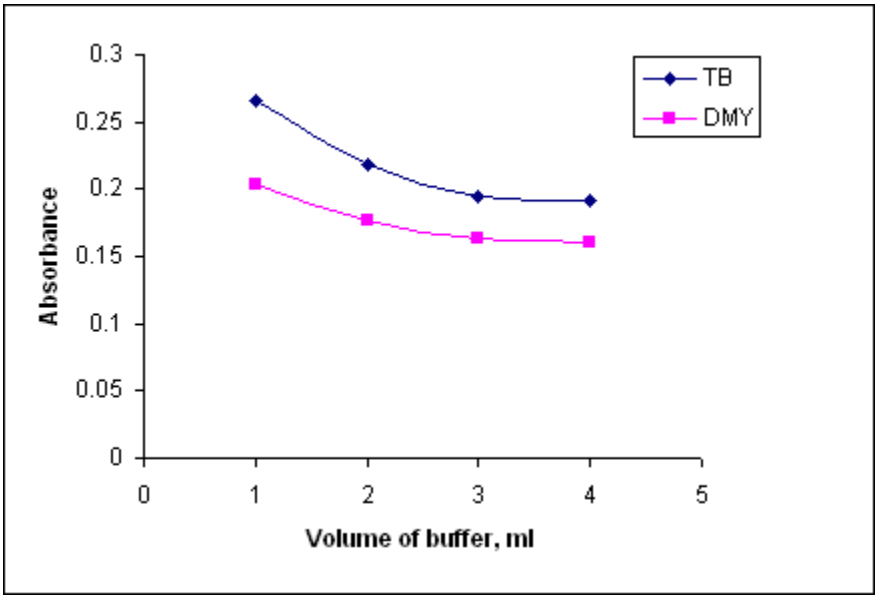

Figure (8): Effect of volume of buffer on the absorbance of chromium **(**VI) using TB and DMY reagents.

Table (10): Effect of reagent concentration on the absorbance of chromium **(**VI) using TB and DMY reagents.

Reagent concentration, mL	**Absorbance**	
	Thymol blue	**Dimethyl yellow**
1	0.111	0.105
1.5	0.192	0.181
2	0.266	0.204
2.5	0.354	0.240
3	0.460	0.255
3.5	0.457	0.252

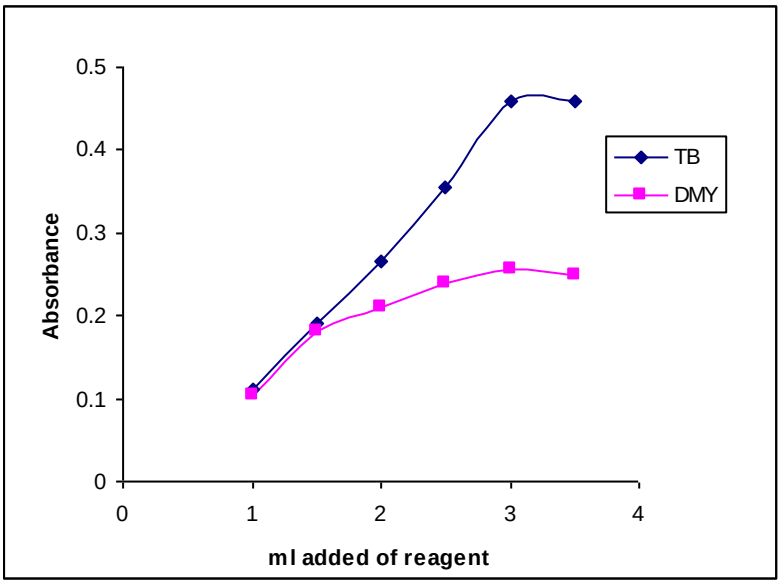

Figure (9): Effect of reagent concentration on the absorbance of chromium **(**VI) using TB and DMY reagents.

Table (11): Effect of sequence of addition on the absorbance of chromium **(**VI) using TB and DMY reagents.

Sequence of addition	**Absorbance**	
	Thymol blue	**Dimethyl yellow**
Buffer + Reagent+Metal	0.160	0.116
Metal+Buffer+ Reagent	0.521	0.230
Reagent+Metal+Buffer	0.462	0.224
Reagent+Buffer+Metal	0.463	0.192
Metal+Reagent +Buffer	0.482	0.260

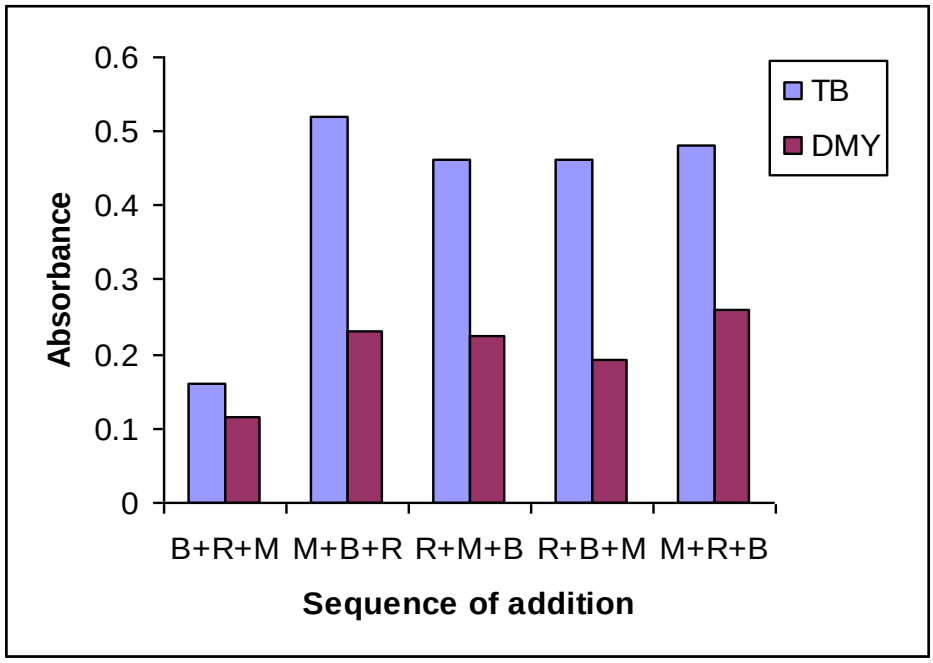

Figure (10): Effect of sequence of addition on the absorbance of chromium **(**VI) using TB and DMY reagents

3.2.1.4. Effect of time and temperature

The effects of time and temperature on metal-reagent complexes were studied by measuring the absorbance of solution containing the metal ion and the reagent in optimum buffer and sequence of addition against blank solution prepared by the same way without metal ion in the visible region at various time and temperature intervals. After studying the effect of time and temperature on the complexes under consideration as shown in

Fig. (11and 12), we found that time and temperature have no effect on the absorbance of chromium (VI) but raising the temperature to 50 C˚ in case of the formed TB complex decrease the absorbance of chromium. These were recorded in Table (12 and 13).

3.2.1.5 Influence of foreign ions

The effect of various ions on the determination of chromium **(**VI**)** was examined by adding chemical standards of Na^{+}, K^{+}, Ca^{+2}, Mg^{+2}, Mn^{+2}, Co^{+2}, Cu^{+2}, Ni^{+2}, Fe^{+3}, Al^{+3}, Ti^{+3} and V^{+3} to 3 µg/mL of chromium **(**VI) . The tolerance limits of interfering species were established at those concentrations that do not cause more than ± 2% error in absorbance values of chromium at 3 µg/ml and data was summarized Table 14. The results indicated that Fe^{+3}, V^{+3}, Ti^{+3} and Mg^{+2} interfere severely in case of using thymol blue reagent but in case of dimethyl yellow reagent Fe^{+3}, V^{+3}, Ti^{+3} and Co^{+2} interfere severely during the measurement of chromium **(**VI**)**.

Table (12): Effect of time on the absorbance of chromium **(**VI) using TB and DMY reagents.

Time, min	Absorbance	
	Thymol blue	Dimethyl yellow
5	0.492	0.259
10	0.491	0.259
15	0.496	0.257
20	0.494	0.253
25	0.495	0.253
30	0.496	0.257

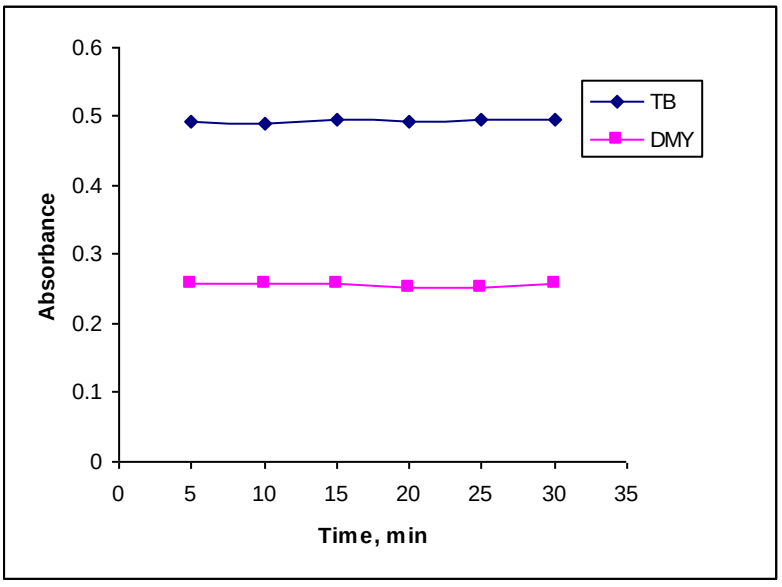

Figure (11): Effect of time on the absorbance of chromium **(**VI) using TB and DMY reagents.

Table (13): Effect of temperature on the absorbance of chromium **(**VI) using TB and DMY reagents.

Temperature, ˚C	**Absorbance**	
	Thymol blue	**Dimethyl yellow**
25	0.490	0.267
30	0.471	0.278
35	0.450	0.267
40	0.462	0.267
45	0.465	0.267
50	0.439	0.268
55	0.428	0.267
60	0.405	0.273

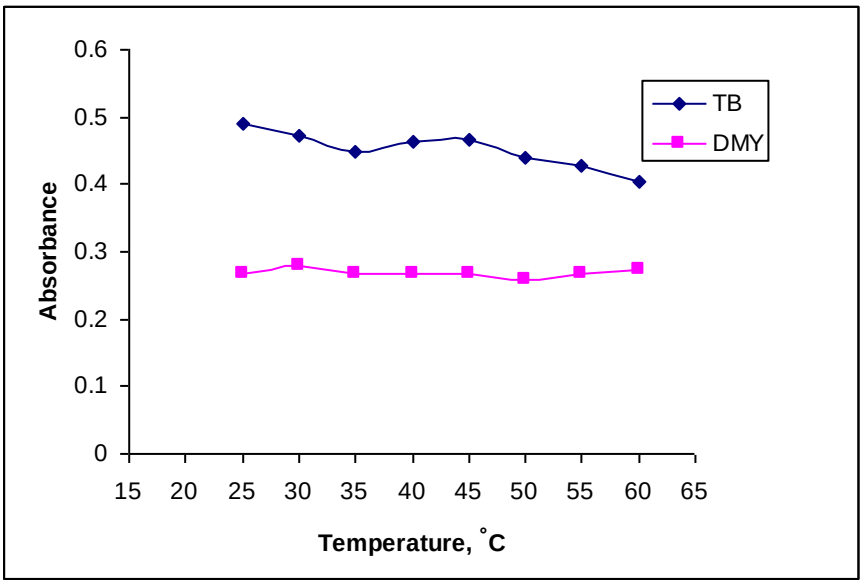

Figure (12): Effect of temperature on the absorbance of chromium **(**VI) using TB and DMY reagents.

Table (14): Tolerance limits for the influence of foreign ions on the formation of Cr complexes with TB and DMY reagents.

Diverse ion added	**Cr-TB** (µg/ml)	**Cr-DMY** (µg/ml)
Na^{+}	200	200
K^{+}	200	200
Ca^{+2}	25	50
Mg^{+2}	5	20
Co^{+2}	15	5
Mn^{+2}	15	10
Zn^{+2}	10	15
Cu^{+2}	25	20
Ni^{+2}	20	15
Fe^{+3}	1	1
Al^{+3}	20	20
Ti^{+3}	5	5
V^{+3}	1	1
Cl^{-}	200	200
Br^{-}	200	200

3.2.2. Mole ratio of Complexes

In order to investigate the molar ratio of the formed complexes between chromium (VI) and reagents under investigation at the selected conditions, the mole ratio and continuous variation methods were carried out. The results showed that the mole ratio between the chromium and used reagents was (1:1), Figures (13 and 14).

3.2.3. Validation of the method

3.2.3.1. Linearity

A linearity study verifies that the sample solutions are in a concentration range where analyte response is linearly proportional to concentration. Under optimum conditions of pH, time, temperature, volume of buffer, reagent concentration and sequence of addition, chromium react with reagents to form complexes, which are often colored and can be subsequently measured colorimetrically. This character is applied for determination of chromium through measuring the absorbance of

the formed colored complex at corresponding optimum wavelength.

Using thymol blue and dimethyl yellow reagents, various parameters affecting the reaction development were studied. A calibration graph was constructed using standard solution of chromium. Under the optimum studied conditions a linear relationship was obtained between the absorbance and concentration of chromium. These were shown in Fig. (15 and 16). Beer's law was verified and found to be satisfactory obeyed for the concentration range (1– 10, 1– 15 μg/mL) for chromium **(**VI**)** using TB and DMY, respectively. This was recorded in Table (15).

Some parameters were calculated in this work by two techniques, these parameters include the correlation coefficient, slopes, intercepts, standard deviation, and relative standard deviation. Also, the molar absorptivity, sandell's sensitivity, detection and quantification limits were calculated from the deviation of the absorbance measurements obtained from Beer's law and recorded in Table (15).

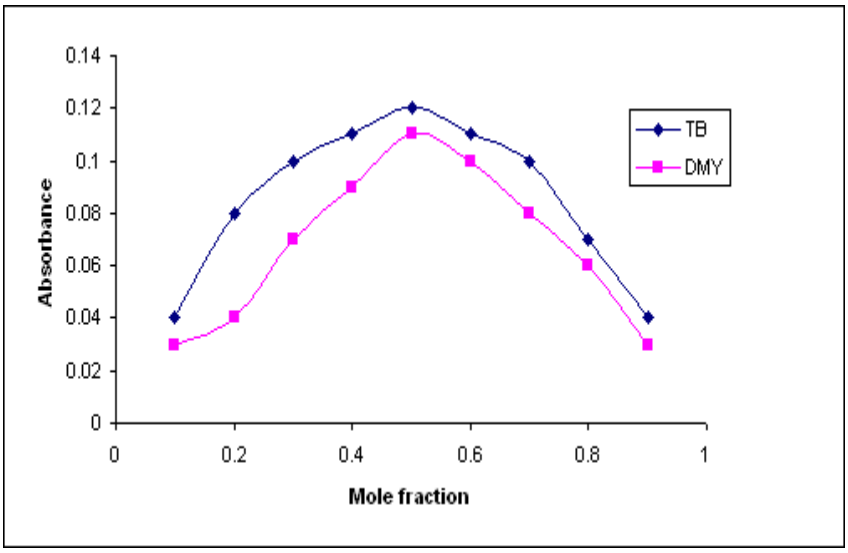

Fig (13): continuous variation method for TB and DMY reagents with chromium **(**VI) under consideration

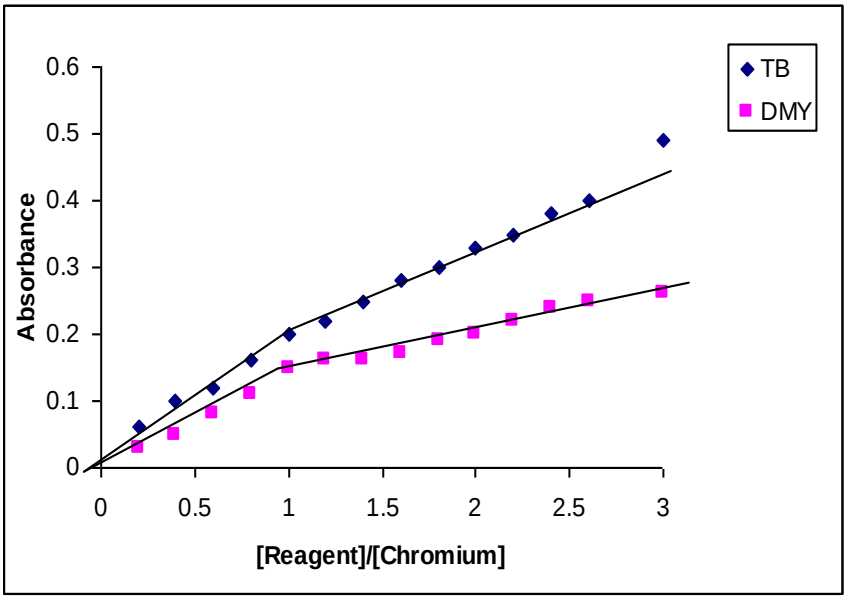

Fig (14): Mole ratio for TB and DMY reagents with chromium **(**VI) under consideration

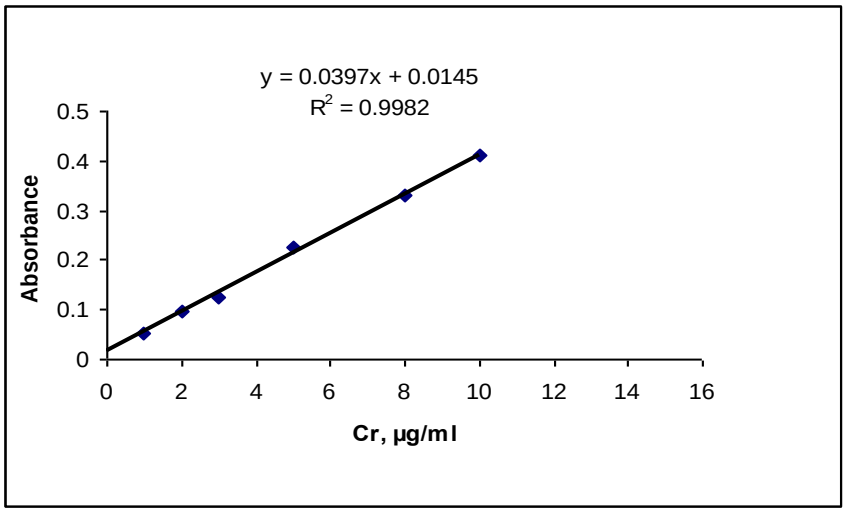

Fig (15): Calibration curve of chromium **(**VI) using thymol blue reagent.

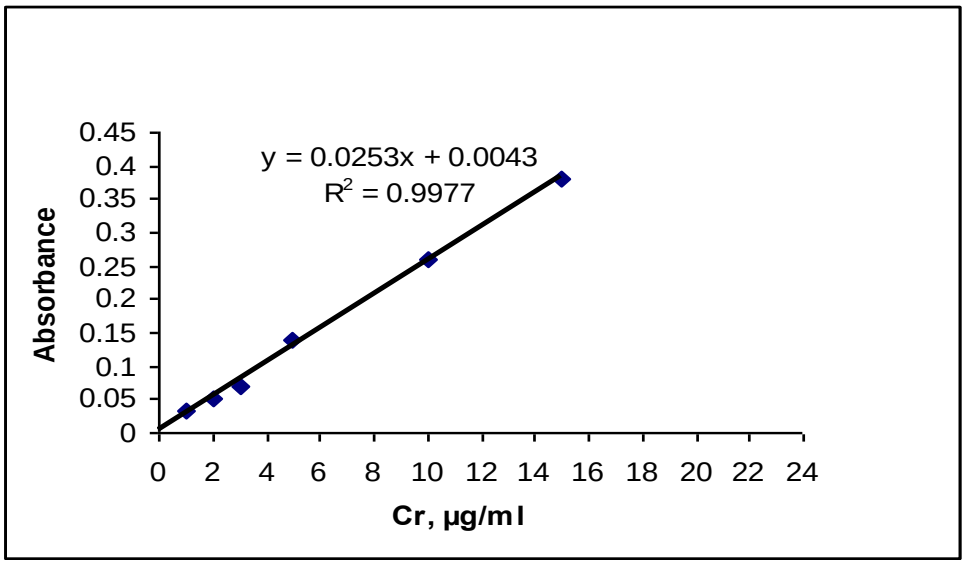

Fig (16): Calibration curve of chromium **(**VI) using dimethyl yellow reagent.

3.2.3.2. Detection and quantification limits

Detection limit of the method is the lowest analyte concentration that produces a response detectable above the noise level of the system, where the quantification limit is the lowest level of analyte that can be accuraly and precisely measured. The repeatability of the method was determined by running six replicated samples, the relative standard deviation was found to be adequate.

3.2.3.3. Accuracy and precision

In order to determine the accuracy and precision of the proposed method, solution containing concentration of chromium was prepared and analyzed in six replicated. The percent standard deviations and the percentage range of error at 95% confidence level were calculated. The results can be considered as very satisfactory, at least for the level of concentrations examined.

Table (15): Analytical data and characteristics of the proposed spectrophotometric and atomic absorption methods for the determination of chromium

Parameters	spectrophotometer		AAS
	TB	**DMY**	
λ_{max} (nm)	548	484	359.7
color	red	yellow	--
pH	2.93	3.76	--
Beer's law limits (µg/ml)	1-10	1-15	0.5-6
Molar absorptivity x 10^4 ($L.mol^{-1}.cm^{-1}$)	0.208	0.129	0.317
Sandell sensitivity (ng / cm^2)	0.025	0.040	0.016
Detection limits (µg/ml)	0.082	0.092	0.054
Quantification limits (µg/ml)	0.250	0.280	0.164
Standard deviation	0.001	0.0007	0.001
Regression equation*: Slop(b)	0.040	0.025	0.061
Intercept (a)	0.014	0.004	0.009
Correlation coefficient (r)	0.998	0.998	0.997
RSD%**	0.78	0.91	0.50
Stoichiometric ratio	1:1	1:1	--

*: With respect to A=a+bC where C is concentration of chromium in µg/ml and (A): is the absorbance, (a): is the intercept, (b): is the slop, and (C): is concentration of chromium in µg/ml.

**: Average of six determinations

3.3. Applications

Due to suppressive effects of Fe^{+3}, Al^{+3}, Cu^{+2}, Co^{+2}, Ni^{+2}, Mg^{+2}, Ba^{+2}, Mn^{+2} and Ca^{+2} on chromium absorbance by atomic absorption method. It was necessary to find a releasing agent to compensate for its effect. 1% Ammonium chloride, 1% ammonium fluoride and 0.2% sodium sulphate were used as masking agents to remove these interferences. In case of spectrophotometer technique, we observed that Fe^{+3},V^{+3},Ti^{+3} and Mg^{+2} interfere in case of using thymol blue reagent but in case of dimethyl yellow reagent, Fe^{+3}, V^{+3}, Ti^{+3} and Co^{+2} interfere during the measurement of chromium (VI).

The proposed atomic absorption method was tested by applying it to the analysis of some international standard rock samples (G-2 (Granite), AGV-1(Andesite), and GSP-1(Granodiorite) [77] by atomic absorption method. Other Egyptian standards [St.4 (Granite), St.5 (Granodiorite), St.6 (Basalt)] [78] were also analyzed and compared with their

certified values. The results of these determinations were given in Table (16). It was found the results obtained were in good agreement with those indicated in literature values and reducible. The procedure could be successfully applied for the analysis of chromium in different variety of samples with satisfactory accuracy and precision.

Table (16): Determination of chromium in International and Egyptian standard rock samples by atomic absorption spectroscopy

Sample	**Certificate values (µg/ml)**	**Present work (µg/ml)**	**Mean (µg/ml)**	**Standard deviation, (µg/ml)**	**Relative Standard deviation,%**
G-2	9	11,10,11,12	11	0.82	7.4
AGV-1	13	14,12,13,12	12.25	0.96	7.5
GSP-1	13	14,13,14,12	13.75	0.96	7.2
St.4	31	32,33,30,32	31.75	1.26	4
St.5	23	22,23,25,23	23.25	1.26	5.4
St.6	46	45,46,44,45	45	0.82	1.8

The proposed atomic absorption method was tested by applying it to the analysis of some collected rock samples from Gabal El Shalol area, S.E.D (South Eastern Desert) Egypt. The chemical analysis of major and trace elements for the collected samples of serpentinite rocks were shown in Table (17).The different contents with chromium element were analyzed in Acme Lab (Canda) using inductivity coupled plasma mass. The results of the chromium obtained by our method show a well match with that obtained by ICP-MS as shown in Table (18). It can be concluded that the proposed method can be applied successfully for analysis of chromium in variety of samples with satisfactory accuracy and precision.

The same method was tested by applying it to the analysis of some minerals ilmenite, synthetic rutile and chromite ore. Ilmenite and synthetic rutile minerals were obtained from the black sand project, Nuclear Material Authority (N.M.A), in which ilmenite was upgraded to a raw titanium base pigment (97% TiO_2). Chromite ore ($FeO.Cr_2O_3$) is the most important mineral occurrence of chromium. The chromite ore sample was obtained

from Anka in Zamfara State which contains 36.84% of Cr_2O_3 [80]. Complete chemical analysis of the major elements analysis was performed using standard methods of analysis and the obtained results were given in the Table (19). These samples were analyzed and compared with their certified values. The results of these determinations were given in Table (20). The data obtained were in good agreement with those indicated in literature values and reducible.

Table (17): Chemical analysis of major and trace elements for serpentinite rocks from Gabble El Shalool area, S.E.D.

Oxides	Sample.1	Sample.2	Sample.3	Sample.4
SiO_2	38.76	39.93	37.72	41.02
TiO_2	00.02	0.05	0.4	0.03
Al_2O_3	0.870	0.65	0.8	0.83
Fe_2O_3	12.42	3.89	4.52	2.53
FeO	00.74	2.94	206	1.16
MnO	00.37	0.13	0.13	0.08
MgO	32.23	37.29	38.34	38.07
CaO	2.810	0.93	1.62	0.75
Na_2O	0.270	0.10	0.05	0.14
K_2O	0.460	0.06	0.03	0.04
P_2O_5	0.880	0.11	0.02	0.01
LOI	8.210	13.76	14.0	15.21
Total	99.66	99.84	99.67	99.88
Cr	1913	3140	1289	1280
Ni	2212	2310	2401	2410
Co	102	96	88	87
V	42	36	34	30
Cu	59	40	10	25
Rb	4	2	4	3
Ba	21	17	21	20

Table (18): Comparison between Cr content in serpentinite rock samples determined by ICP-MS and AAS.

Sample	Certificate values by ICP-MS (Acme Lab)* (µg/ml)	Present work by AAS (N.M.A) (µg/ml)	Mean (µg/ml)	Standard deviation, (µg/ml)	Relative Standard deviation,%
1	1913	1901,1903,1905, 1903	1903	1.6	0.08
2	3140	3135,3133,3132, 3134	3133.5	1.3	0.04
3	1289	1279,1280,1282, 1280	1280.2	1.5	0.12
4	1280	1279,1282,1278, 1279	1279.5	1.7	0.13

* The certified samples were analyzed in Acme Lab. Canada

Table (19): Major elements analysis of minerals under study by atomic absorption spectroscopy

Element Oxide	Rosetta Ilmenite	Chromite ore	Synthetic Rutile
SiO_2	0.50	13.74	0.60
TiO_2	46.50	0.32	97.00
Fe_2O_3	49.91	21.51	1.50
CaO	0.44	2.24	- -
MgO	0.80	14.00	0.40
V_2O_5	0.18	- -	0.15
Al_2O_3	- -	11.00	- -
MnO	1.15	0.3	- -
Cr_2O_3	0.29	36.84	0.08
Total	99.77	99.95	99.73

Table (20): Chemical analysis of chromium in minerals under investigation by atomic absorption spectroscopy

Mineral	Published data[79, 80] (Cr_2O_3) (µg/ml)	Present work (Cr_2O_3) (µg/ml)	Mean (µg/ml)	Standard deviation, (µg/ml)	Relative Standard deviation,%
Rosetta Ilmenite	0.29	0.32,0.30,0.33.0.32	0.32	0.01	3.1
Chromite ore	36.84	36.9,36.5,37,36.6	36.75	0.238	0.65
Synthetic Rutile	0.0778	0.06,0.05,0.06,0.07	0.06	0.008	13.3

The proposed spectrophotometry methods were tested by applying it to the analysis of some water samples (drinking water, ground water and wastewater). The drinking water was obtained from the Tap of lab from Nuclear Materials Authority, the ground water was obtained from Bir El Shalol, S.E.D, Egypt and the wastewater was obtained from the project of phosphoric acid purification at Nuclear Materials Authority. These water samples were analyzed and the results of these determinations were given in Table (21). The precision of the proposed method was evaluated by replicate analysis of samples containing chromium at six different concentrations.

Table (21): Chemical analysis of chromium (VI) in water samples under investigation by spectrophotometry using TB and DMY reagents.

Sample	Proposed method using TB reagent					Proposed method using DMY reagent			
	Cr in µg/mL added	Cr in µg/mL found[a]	Std deviation	Recovery, %	t-test[b]	Cr in µg/mL found[a]	Std deviation	Recovery, %	t-test[b]
Drinking water	4.0	4.02	0.04	100.5	1.22	4.04	0.05	101.0	1.96
	6.0	5.96	0.05	99.3	1.96	5.98	0.04	99.6	1.22
Ground water	4.0	4.03	0.05	100.7	1.47	4.02	0.03	100.5	1.63
	6.0	5.99	0.04	99.8	0.61	6.02	0.05	100.3	0.98
Waste water	4.0	3.98	0.05	99.50	0.98	4.04	0.05	101.0	1.96
	6.0	6.04	0.06	100.6	1.63	5.97	0.06	99.3	1.49

[a] Average of six determination

[b] Tabulated t-value for 5 degree of freedom at 95% confidence level is 2.57 .