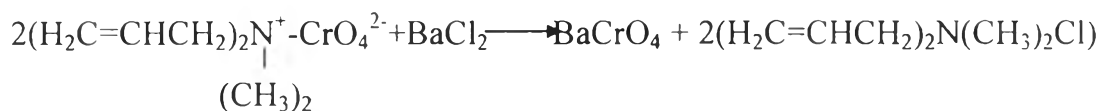# CHAPTER IV
RESULTS AND DISCUSSION

4.1 Equilibration Time

Two experimental conditions were used to cover the range of conditions used in this study. The first experiment used 0.1 M QUAT, 0.002 M CrO_4^{2-}, and 0.002 M Ba^{2+} and the second experiment used 0.4M QUAT, 0.8M CrO_4^{2-}. and 0.4M Ba^{2+}. The plot of percentage of chromate precipitated as a function of time are shown in Figure 4.1.

These results showed fluctuation in the initial region time probably because of microcrystals in supernatant. The results showed that the equilibrium was reached after 24 hours at 30 $^{\circ}$C. As the result, the equilibrium time of 48 hours was used in all experiments.

4.2 Equilibrium Precipitation

The precipitation reaction may be given as follows,

$$2(H_2C=CHCH_2)_2\overset{+}{\underset{|}{N}}\text{-}CrO_4^{2-} + BaCl_2 \longrightarrow BaCrO_4 + 2(H_2C=CHCH_2)_2N(CH_3)_2Cl)$$
$$(CH_3)_2$$

The precipitation can be achieved by adding excess barium over the stochiometric requirements. As the result, the ratio of barium to chromate was from 1 to 10. This work was divided into 3 experiments. First, it was studied
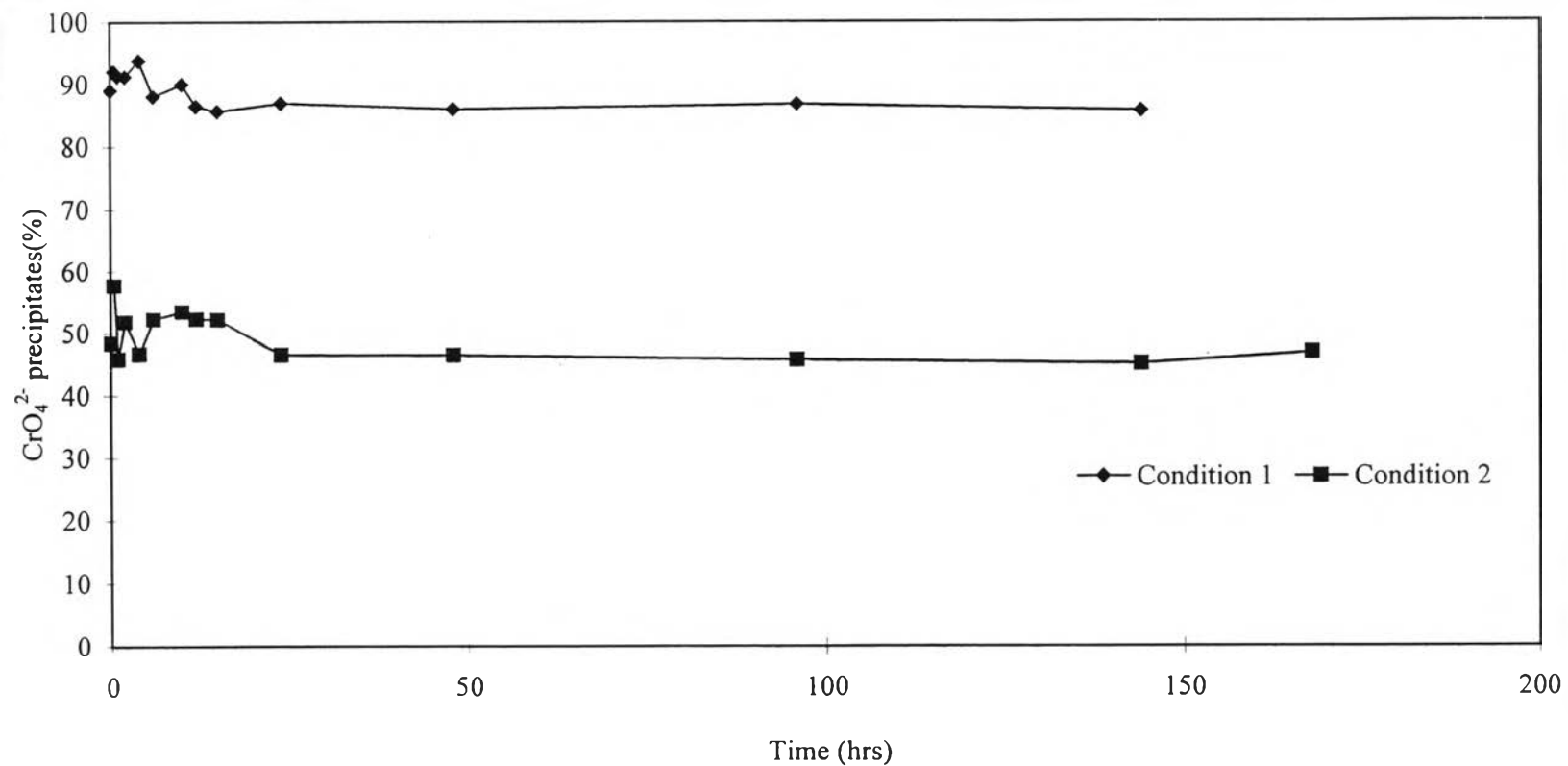
Figure 4.1   Precipitation equilibrium of barium chromate

Note : Condition 1 : Initially, the concentrations of chromate, barium ions and QUAT were 0.002 M, 0.002M,
and 0.1 M , respectively.
Condition 2 : Initially, the concentrations of chromate, barium ions and QUAT were 0.8 M, 0.4M, and 0.4 M,
respectively.

the effect of chromate concentration on barium chromate precipitation while holding the concentration of barium ions constant at 0.08 M and fixing the concentration of QUAT 0.1, 0.2, 0.3, and 0.4 M is shown as plots of percentage of chromate ions remaining in the solution as a function of the concentration ratios of barium to chromate in Figure 4.2 and Table 4.1.

From the observed results (Figure 4.2), chromate in high QUAT concentration was more than that of lower concentration, especially it was compared with absence QUAT condition, i.e. chromate remaining in presence 0.1 M and 0.4 M QUAT was approximately 3 and 4 times of in the absence QUAT, respectively. But the results were slightly changed in the excess barium condition. These results showed that the increase of QUAT concentration led to more chromate ions in supernatant because of QUAT binding. Therefore, excess barium was necessarily added for completion with QUAT in order to form barium chromate precipitate.

Second, the effects of barium concentration on the barium chromate precipitation were studied by setting the QUAT concentration constant at 0.1 M. Also, the concentrations of chromate ions were kept constant at 0.002, 0.02 and 0.06 M. The results as the plots of chromate ions remaining in supernatant as a function of the concentration ratios of barium to chromate were shown in Figure 4.3 and Table 4.2.

In Figure 4.3, when the ratio of barium to chromate was 1, barium ions remaining in high concentration of chromate ions were less than that of the low concentration because of the difference between the concentration ratios of QUAT to initial chromate ions. The ratios of QUAT to chromate were 50 for 0.002 M CrO_4^{2-} and 1.67 for 0.06 M CrO_4^{2-}. The results showed the influence of QUAT binding on the solubilization of barium chromate. Therefore, the solution contained high concentration of barium ions at the high QUAT to chromate ratio.
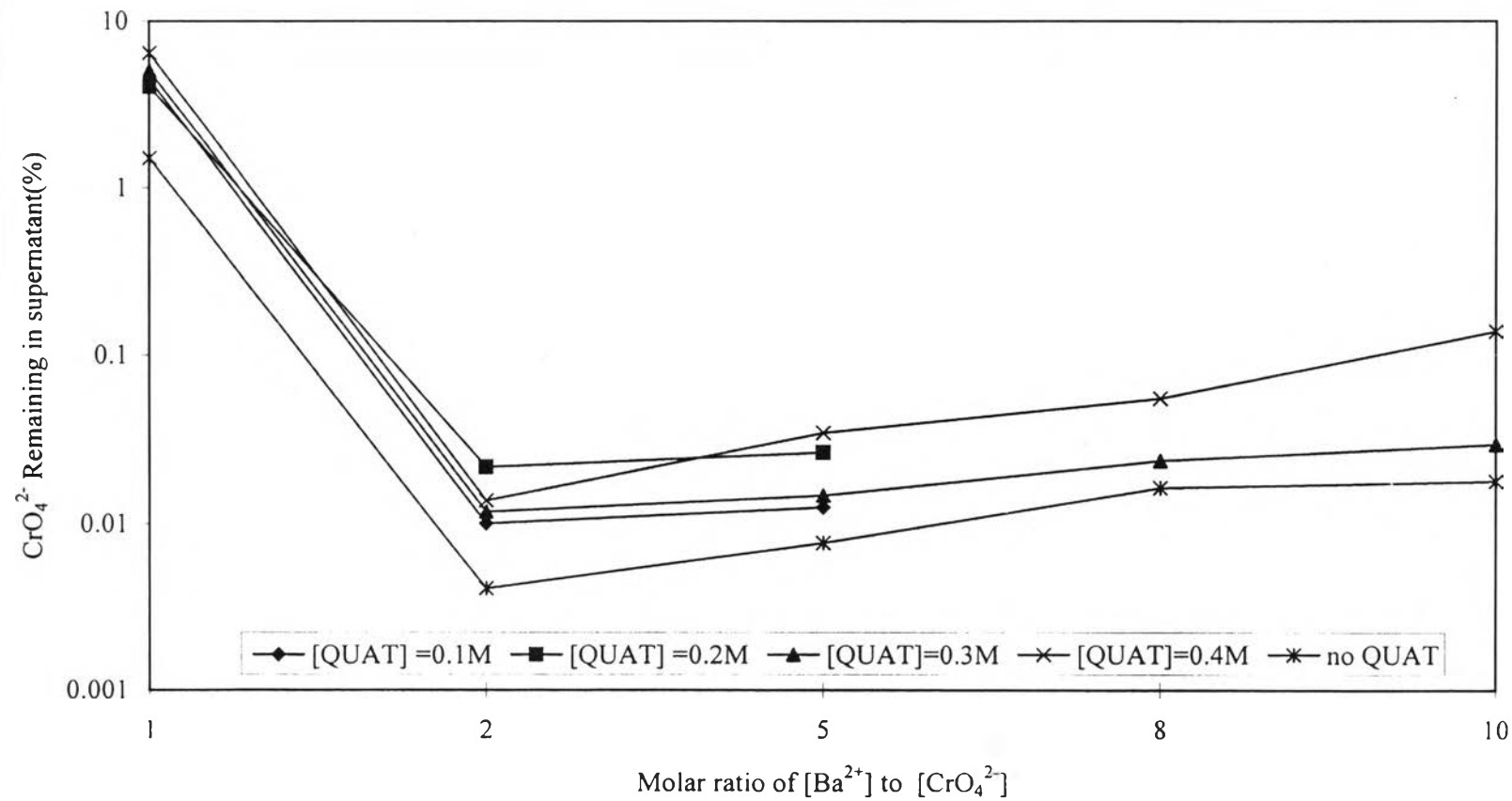
Figure 4.2 Fraction of CrO_4^{2-} (%) in supernatant with initial $[Ba^{2+}] = 0.08$ M.

Table 4.1   Percentage of barium chromate precipitated when the chromate
concentrations were varied from 0.008 to 0.08 M and the barium
concentration was fixed at 0.08 M

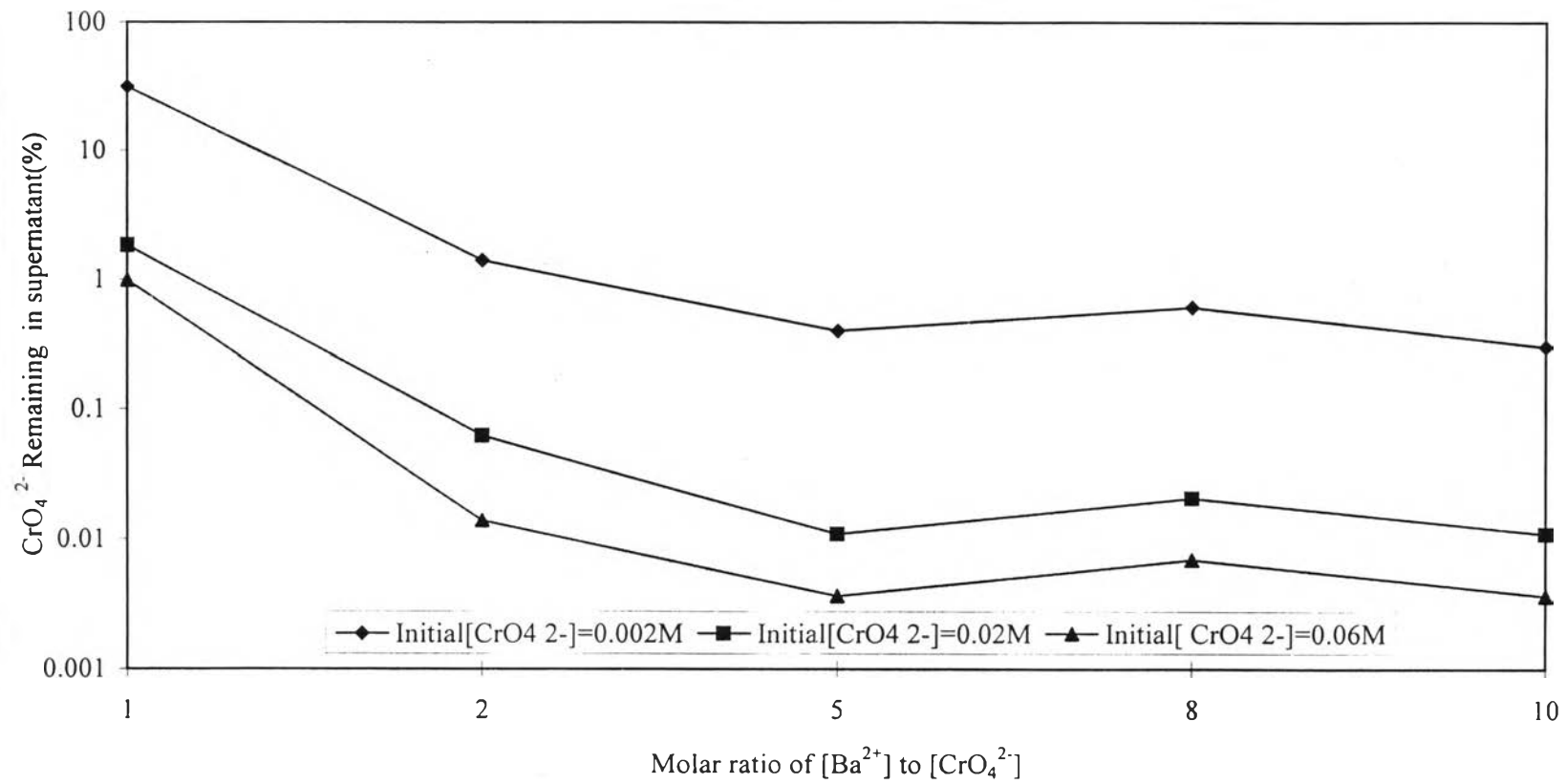| Initial condition				% CrO_4^{2-}
[QUAT]:M	$[CrO_4^{2-}]$ / [QUAT]	[CrO_4^{2-}]:M	$[Ba^{2+}]/[CrO_4^{2-}]$	precipitate
0.1	0.800	0.080	1	95.5163
0.1	0.400	0.040	2	99.9900
0.1	0.160	0.016	5	99.9875
0.1	0.100	0.010	8	100.0000
0.1	0.080	0.008	10	100.0000
0.2	0.400	0.080	1	95.9720
0.2	0.200	0.040	2	99.9783
0.2	0.080	0.016	5	99.9735
0.2	0.050	0.010	8	100.0000
0.2	0.040	0.008	10	100.0000
0.3	0.267	0.080	1	94.9598
0.3	0.133	0.040	2	99.9882
0.3	0.053	0.016	5	99.9852
0.3	0.033	0.010	8	99.9763
0.3	0.027	0.008	10	99.9704
0.4	0.200	0.080	1	93.5641
0.4	0.100	0.040	2	99.9862
0.4	0.040	0.016	5	99.9655
0.4	0.025	0.010	8	99.9448
0.4	0.020	0.008	10	99.8620
0	0.000	0.080	1	98.4991
0	0.000	0.040	2	99.9959
0	0.000	0.016	5	99.9923
0	0.000	0.010	8	99.9836
0	0.000	0.008	10	99.9820

Figure 4 .3   Fraction of CrO_4^{2-} (%) in supernatant with [QUAT] = 0.1 M.

Table 4. 2   Percentage of barium chromate precipitated when the
barium concentrations were varied from 0.002 to 0.2 M
and the QUAT concentration was fixed at 0.1 M

Initial condition				%CrO$_4^{2-}$
[CrO$_4^{2-}$] / [QUAT]	[CrO$_4^{2-}$]	[Ba^{2+}]/[CrO$_4^{2-}$]	[Ba^{2+}]	precipitate
0.02	0.002	1	0.002	68.1019
0.02	0.002	2	0.004	98.5993
0.02	0.002	5	0.010	99.6027
0.02	0.002	8	0.016	99.3940
0.02	0.002	10	0.020	99.7020
0.20	0.020	1	0.020	98.1731
0.20	0.020	2	0.040	99.9374
0.20	0.020	5	0.100	99.9891
0.20	0.020	8	0.160	99.9791
0.20	0.020	10	0.200	99.9891
0.60	0.060	1	0.060	99.0155
0.60	0.060	2	0.120	99.9861
0.60	0.060	5	0.300	99.9964
0.60	0.060	8	0.480	99.9930
0.60	0.060	10	0.600	99.9964

The last effect of QUAT was studied by varied the concentration of QUAT from 0.1 to 0.4 M, fixed the barium concentrations 0.02, 0.04, 0.1, 0.16 and 0.2 M and the chromate concentration was 0.02 M. The results showed as the plots of the percentage of barium and chromate remaining in supernatant as the function of the QUAT concentration are illustrated in Figure 4.4 and Table 4.3.

Figure 4.4 showed that at concentration ratio of barium to chromate equal 1, the percentage of chromate remaining in supernatant increased obviously when the observed results in the absence of QUAT were compared with in the presence 0.1 M QUAT or the QUAT increasing from 0.1 M to 0.4 M.

According to material balance, CrO_4^{2-} precipitate could be obtained from equation (1).

$$[CrO_4^{2-}]_{Precipiate} = [CrO_4^{2-}]_{Initial} - [CrO_4^{2-}]_{Supernatant} \text{------------(1)}$$

where $[CrO_4^{2-}]_{Initial}$ is the initial concentration of chromate ions.

$[CrO_4^{2-}]_{Supernatant}$ is the remaining concentration of chromate ions after equilibrium conditions.

Table 4.1, 4.2, and 4.3 were demonstrated the percentage of chromate precipitated in form barium chromate under equilibrium conditions for various Ba^{2+}, CrO_4^{2-}, and QUAT concentrations.

In Table 4.1, according to the stoichiometric of barium chromate formation ($[CrO_4^{2-}] = 0.08$ M, $[Ba^{2+}] = 0.08$ M), 98% of chromate was precipitated in the absence of QUAT condition. As the result, it showed that precipitation process was effective for chromate separation. It was quite similar to previous study (Tucker et. al., 1992). However, the percentage of
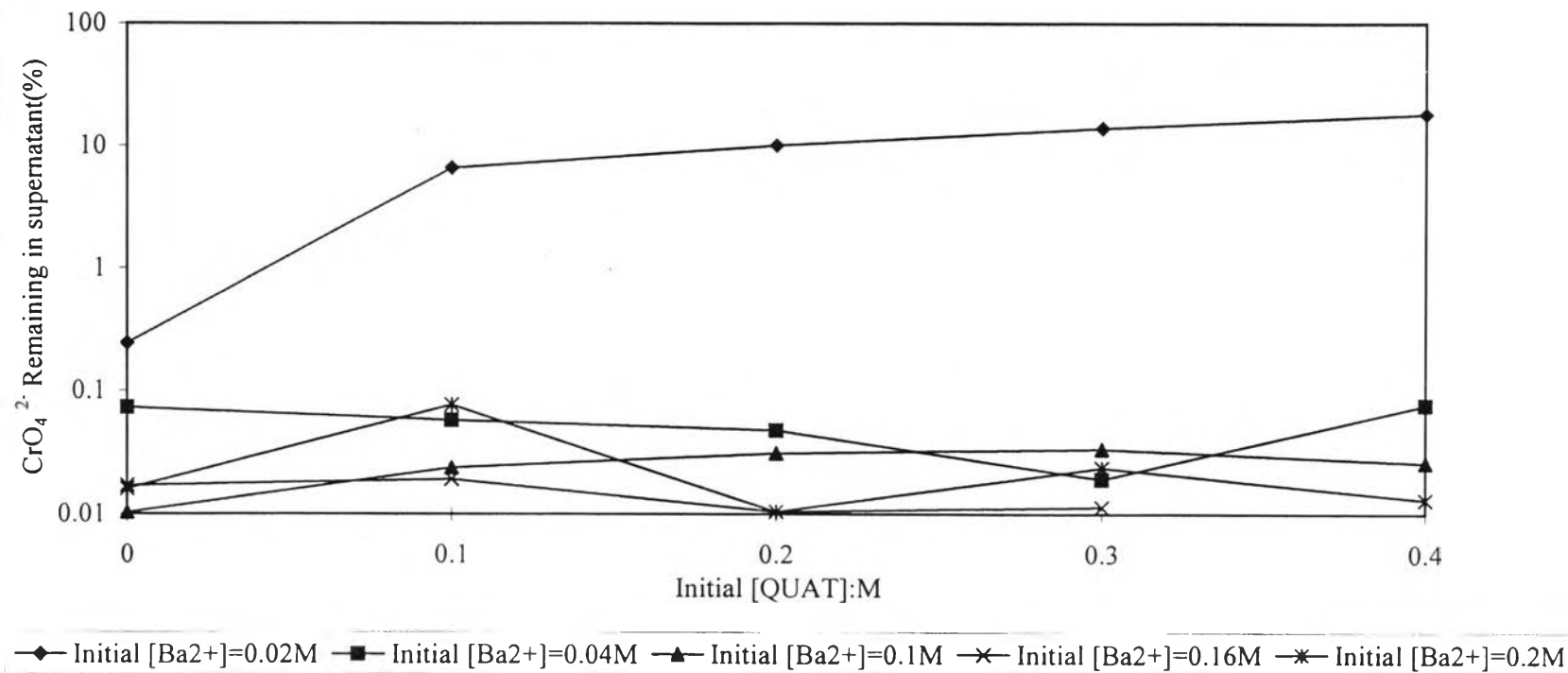
Figure 4.4 Fraction of CrO_4^{2-} (%) in supernatant with initial $[CrO_4^{2-}]$=0.02 M.

Table 4.3 Percentage of barium chromate precipitated
when the QUAT concentrations were varied from
0.1 M to 0.4 M and the chromate concentration
was fixed at 0.02 M

Initial condition			% CrO_4^{2-}
[QUAT]	$[CrO_4^{2-}]$ / [QUAT]	$[Ba^{2+}]/[CrO_4^{2-}]$	precipitate
0.1	0.20	1	93.4528
0.2	0.10	1	89.9691
0.3	0.07	1	86.1153
0.4	0.05	1	82.0055
0.1	0.20	2	99.9424
0.2	0.10	2	99.9371
0.3	0.07	2	99.9204
0.4	0.05	2	99.9738
0.1	0.20	5	99.9520
0.2	0.10	5	99.9685
0.3	0.07	5	99.9659
0.4	0.05	5	99.9738
0.1	0.20	8	99.9808
0.2	0.10	8	99.9895
0.3	0.07	8	99.9886
0.4	0.05	8	100.0000
0.1	0.20	10	99.9232
0.2	0.10	10	99.9895
0.3	0.07	10	99.9761
0.4	0.05	10	99.9869
0		1	99.7579
0		2	99.9271
0		5	99.9897
0		8	99.9829
0		10	99.9840

chromate precipitated decreased to 95 % and 93 % in the presence of 0.1 M QUAT and 0.4 M QUAT, respectively. The results showed the influence of QUAT on the barium chromate precipitate. With greater than a stoichiometric of BaCl$_2$ added (the ratio of barium to chromate were 2, 5, 8, and 10), the chromate precipitate was in the range of 99 %. As the results, the barium chromate beated the QUAT binding down.

From the observed results in Table 4.2, when the ratio of barium to chromate was 1, they showed obviously the effect of concentration of QUAT. The percentage of chromate precipitated decreased from 93 % to 82 % as increasing in the QUAT concentration from 0.1 M to 0.4 M. However it was less than the previous condition because of the less initial concentration of chromate.

The solubility product constant (K$_{sp}$) of barium chromate in this work could be not obtained because either [Ba^{2+}] or [CrO$_4^{2-}$] was always too low to analyze with an atomic absorption spectrophotometer. Futhermore, the 1:1 ratios should give roughly equal [Ba^{2+}] and [CrO$_4^{2-}$] in the supernatant, but there was always a lot of [CrO$_4^{2-}$] left over in the 1:1 cases. However, E.E. Tuker's studies had shown that K$_{sp}$ of barium chromate was equal to 1.2×10^{-08}.