LIQUID-LIQUID EXTRACTION OF CHROMIUM BY DIPHENYL-2-PYRIDYLMETHANE

by

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EXTRACTION OF CHROMIUM BY DIPHENYL-2-PYRIDYLMETHANE

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ABSTRACT

The liquid-liquid extraction of chromium from aqueous solutions of hydrochloric acid by diphenyl-2-pyridylmethane (DPPM) dissolved in hydrogen-bonding organic diluents has made possible the separation, concentration and speciation of chromium at trace concentrations.

In the extraction of Cr(VI) the most effective diluents employed were, in order: CH_2ClCH_2Cl, CH_2Cl_2 and $CHCl_3$. While Cr(VI) was extracted best from HCl solutions the actual order of extraction of the inorganic acids themselves, used in the protonation of the DPPM, was found to be: $HClO_4 > HNO_3 > HBr > HCl > H_2SO_4, H_3PO_4$. The extraction of Cr(VI) was followed by using commercial high specific activity ^{51}Cr or enriched material prepared by a Szilard-Chalmers reaction. The distribution ratio (D) in all 0.10M DPPM/diluent extractions increased with an increase in the acid concentration up to about 1M in HCl but decreased thereafter.

To account for the extraction a model is proposed which suggests that the distribution of Cr(VI) depends mainly upon the availability of $DPPMH^+$ in the aqueous phase and the form of the Cr(VI). Both the model and spectral evidence support the extraction of the CrO_3Cl^- species.

With the large separation factors available, Cr(VI) may be separated from inorganic Cr(III), organic Cr(III) complexes, such as $Cr(C_2O_4)_3^{3-}$, and many other metallic species. Total chromium in the aqueous sample may be determined by an analysis of the extract after a Ce(IV) oxidation. Further, with a distribution ratio as high as D ≈ 700, it is possible to concentrate the chromium from an aqueous sample to facilitate the

analysis in the simplified matrix of the organic phase.

This extraction may overcome the problems associated with chromium analysis at trace concentrations, where samples are so subject to loss by adsorption or changes in oxidation state upon storage. While back extractions have been examined, the direct analysis of the chromium in the extract by atomic absorption (ng/mL concentrations) or spectrophotometric (µg/mL concentrations) methods is advocated.

for
Patricia,
Carissa and Chandra

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In my efforts to understand I have had a great deal of assistance. In this endeavor I would like to recognize particularly:

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The product of mental labor - science always stands far below its value, because the labor-time necessary to produce it has no relation at all to the labor-time required for its original production.

Karl Marx

I. INTRODUCTION

1.1 The Significance of Chromium

While chromium (III) is an essential trace substance, chromium (VI) is highly toxic. Thus, a concern about chromium not only in the work place but also in the environment is justified. Unfortunately, the public can become unduly alarmed when press reports such as that released by Pollution Probe mention chromium as a prominent carcinogen in water supplies derived from Lake Ontario[1] or a magazine pictures polluted waters with the caption "chromium in stream can cause cancer".[2] Chemists must bear some of the responsibility for any misunderstanding about the significance of chromium in the environment. Analytical advances may now permit an analysis, albeit with difficulty at very low concentrations in the complicated matrix of some natural waters, but speciation is seldom reported. This situation prompted the initial interest in exploring procedures which could not only facilitate the analysis by separating and concentrating the chromium in aqueous systems but also permit speciation.

The role of chromium as an essential trace element in man was first established in 1959 by Schwartz and Mertz.[3] The subsequent major review by Mertz[4] and the recent monograph by Saner[5] provide a current perspective on the biological significance of chromium. Occurring as Cr(III), it is implicated in lipid metabolism, protein synthesis and, in

a major way, glucose metabolism.[4,5,6,7] Chromium deficiency, while rare, has been correlated with a number of medical problems.[5] It has been suggested that the North American diet, possibly because of the access to highly refined foods, may not provide for optimal chromium nutrition.[5,8,9] Supplementation has been advocated, particularly for the elderly[10], but the effectiveness of the chromium administered depends upon its form[4,5,8,9] - biologically active sources include brewers yeast, certain red meats and beer.[9]

Although essential as a trace element, chromium can exhibit harmful properties, particularly as Cr(VI). It is listed as a carcinogen or suspected carcinogen associated with specific occupations.[11,12,13,14] It can cause skin allergies, dermatitis and ulceration in man under certain conditions.[8,15] The long term effect of exposure to trace amounts is unclear.

Animal studies indicate that ingestion of Cr(VI) can cause tissue damage, although Cr(III) is comparatively safe.[5] It has also been reported that chromium is more toxic to fish than is lead and appears to be toxic to algae at trace levels.[8] According to Volkovic[16] there are numerous reports of toxic effects on plants yet it is a common trace constituent therein (a mean value of 0.5 µg/g is reported for dried plant material in southern Ontario[17]).

Of further concern is the fact that neither the forms of chromium nor the process by which biological systems take it up are well understood. Frausto da Silva and Williams[18] decry the deficiency of analysis which has failed to establish which complexes at low concentrations are involved. They point out that the uptake route

cannot be the same as that for iron or manganese, but probably involves Cr(III) complexes of RO^- anions (enolates, phenolates, etc.) at some stage.

1.2 Trace Analysis of Chromium

1.2.1 Analytical Methods

The problem of determining the total concentration of chromium in natural waters or biological fluids can in itself be a challenge, without even considering the speciation. For instance, in a national survey of trace elements in Canadian drinking water supplies the median and range concentrations of chromium were found to be: Cr≤2.0 (≤2.0 - 8.0) ng/mL.[19] This was reported as being near the detection limit of 2 ng/mL for the analysis by graphite furnace atomic absorption spectrometry (GFAAS). Biological fluids such as blood or urine present at least as many difficulties in analysis. The diverse range of values for blood chromium reported in the literature is an indication of how little confidence can be placed upon any analytical procedure let alone the norm.[5] Again, with urine, the major excretory pathway of absorbed chromium[4,5], there is no accepted range which might reflect an optimum health status, primarily because the analytical methodology has not been developed to an acceptable level.

Currently, atomic absorption techniques involving electrothermal atomization (ETA-AAS) are favoured in the analysis of chromium at trace concentrations. In 1980 Berman[15] recommended this method for analysis of samples directly or after pre-treatment, but with a reservation:

"For the most part, the direct analysis techniques described are of little merit". Tessari and Torsi[20] also recommended the technique for clinical and environmental samples because of the high sensitivity, small sample size, freedom from interference by major constituents, simplicity and rapidity.

More recent reports place the direct analysis by ETA-AAS in an improved perspective; an indication of the general improvements in the last decade[21] or the progress in background corrections.[22] Biological fluids have been examined directly with quite reasonable agreement among researchers. The normal level of chromium in urine is now thought to be below 1 ppb (1 µg/L),[23,24,25] a value which is more consistent with the dietary intake and balance than the higher levels once considered normal in urinary excretions.[26] Blood analysis has also improved[24], although it is far from being routine. For environmental samples, while direct analysis is possible[19,27], it may be of importance to include a pre-treatment which permits speciation.

Alternative analytical approaches have more limited applications. Mass spectrometry can provide for extreme sensitivity but is somewhat complex for routine use[28]. It has been used to determine chromium in sea water[29] and urine[30]. Both instrumental and destructive neutron activation analyses have been employed, particularly in attempts to develop standard reference materials in biological matrices because chromium determinations are in such a "sad state".[31] Without a preconcentration step the techniques are not sufficiently sensitive for reliable determinations in natural waters or biological fluids.[32] A spectroscopic technique of promise uses inductively coupled plasma, but

again, a preconcentration step is required.[33] Older spectrophotometric (colorimetric) methods, particularly those involving diphenylcarbazide, have some specific applications[34,35,36]. Different colorimetric reagents[37] or the use of the Cr(VI) absorption itself[38] also have been utilized.

Although there have been improvements in the analysis of chromium at trace levels an examination of recent papers reveals the state of achievement and comparative results for different methodologies. Versieck and Cornelis[39], in their review, point out that the inconsistent chromium values obtained in National Bureau of Standards' samples prove that most published values are in error. De Goeij et al.[40] also examined the problems in establishing the levels of chromium in biological reference materials. At best an "information value only" could be given for a sample such as milk powder because of the scatter and range of values reported. No current analytical technique was satisfactory and some methodologies yielded obviously high values.

1.2.2 Preconcentration, Separation, Speciation

While the direct analysis of total chromium is feasible with some samples, there is more often a preliminary stage in the analytical scheme in which the analyte is concentrated. With biological samples ashing before analysis is common. This ashing precludes the speciation of chromium in the original sample. On the other hand, for many environmental samples there have been schemes developed which permit not

only the concentration of chromium but also, with varying degrees of success, its separation from interfering elements and its speciation.

Before the trace chromium analysis of environmental samples, such as natural waters, the particulate matter, including particulates containing chromium, is removed by a physical separation technique. This usually involves filtration through a 0.45 μm millipore membrane filter. If one examines the recent review by De Mora and Harrison[41] on the physical separation techniques in trace metal speciation studies, it becomes obvious that this separation could have an influence on the chromium content in the solution to be analyzed. Since the sampling itself can be so crucial to the subsequent analysis it is advisable to adopt a standard procedure such as that ascribed to by Environment Canada.[42]

If only the total dissolved chromium in an aqueous sample is of interest the solution may be stabilized by dilute HNO_3 and saved for later laboratory analysis. However, if speciation is of interest a separation/preconcentration step must be performed immediately. The currently favoured methods involve coprecipitation, solvent extraction or ion-exchange. Although the subsequent analysis could be accomplished by several of the methods mentioned previously, the most common choice is by AAS.

Ion Exchange

Although ion-exchange methods have been extensively employed in the analysis of chromium there are certain limitations when they are used in trace analysis schemes. There is a growing recognition that it is difficult to achieve quantitative exchange and separation of the

various ionic forms of chromium and an even greater problem in assuring complete elution from a resin. Several recent reports demonstrate both the usefulness and limitations of such methods.

Sylvester and co-workers[43] were particularly concerned about the release of highly toxic chromate-based corrosion inhibitors in the blowdown water from industrial cooling towers. Macroreticular anion-exchange resins in the Cl^- form most favourably adsorbed the Cr(VI) in the pH range of 4.8 to 5. There was a dramatic drop in capacity below pH 5 and below pH 4 an actual reduction of Cr(VI), possibly because the oxidizing power became great enough to attack the resin. The effect of NaCl being present up to 3000 ppm was minor but salt concentrations exceeding this value limited the success of the exchange. It is obvious that for Cr(VI) separations even the most effective resins have a limited pH working range and are subject to interference problems.

Cresser and Hargitt[44] found that Cr(VI) would adsorb to only 97% on their anion-exchange resins when at trace levels. At the same time, in the presence of oxalate and citrate anions, there was an adsorption of Cr(III) on to the resin. It seems that anion-exchange resins cannot be used to quantitatively separate Cr(VI) at trace levels and are not reliable in selectively speciating Cr(VI) in the presence of organic complexing agents.

Greenberg and Kingston[45] found other difficulties when using chelex-100 resin to concentrate Cr and other trace elements from seawater for subsequent neutron activation analysis. First, it was recognized that to try to elute the chromium reproducibly let alone

quantitatively would not be successful. Irradiation of the sample chromium trapped on the resin could be done readily and an accurate analysis performed if the salt matrix could be reduced sufficiently. Therefore, to avoid the elution problem with chromium a number of washes with water and with ammonium acetate were used to selectively elute the alkali and alkaline earth metals. However, significant quantities of chromium were lost in the buffer elution. They suggested that this loss, not previously recognized, could be due to changes in the ionic form or oxidation state. As a consequence, the trace analyses of chromium using chelex-100 and employing the techniques described must be regarded as less than ideal.

Recently Isozaki et al.[46] investigated the use of chelex-100 for Cr(III) analysis. Cr(III) at the $\mu g\ L^{-1}$ level was quantitatively adsorbed from solution at pH 4.0. The resin was collected, suspended in an aqueous slurry and injected directly into a carbon furnace in an ETA-AAS determination. The filtrate containing Cr(VI) was reduced by HCl and H_2O_2, then analyzed as before. Common ions, except Al and Fe, did not influence the determination of chromium. Although this investigation was with a synthetic mixture it is expected that the determination of Cr(III) and Cr(VI) in natural waters will prove feasible.

Orvini and Gallorini[47] also tried to overcome the elution difficulties on resins by trapping the various chromium species from river waters and analyzing for chromium on the resin by neutron activation methods. At an operational pH of 5.5 they successively trapped the Cr(III) on AG50W-X4 (H^+) resin then the Cr(VI) on

AG1-X4(OH^-) resin. The eluate was saved for the determination of non-ionic chromium. They claimed that under their conditions ionic Cr(III) was retained quantitatively on the cation-exchange resin, Cr(VI) passed through it to be retained quantitatively on the anion-exchange resin, and that a number of complexing agents did not influence the behaviour of the chromium ions on the resin system.

Several Japanese researchers[48,49,50,51] have reported a spectrophotometric analysis involving ion-exchange procedures which makes it possible to determine the chromium content, after oxidation, in some natural waters. The diphenylcarbazide complex of Cr(VI) is trapped on resin particles so as to enhance the color density sufficiently to permit analysis down to 1×10^{-8} M.

Spectrophotometric detection of chromium has advanced to the point where it is being applied in a number of newer instrumental methods. Approaches involving ion-chromatography seem of great potential but are not yet applicable at the ppb concentration region.[52] Fritze and Sikafoose[53] have reported a rapid instrumental liquid chromatographic procedure as well. Using macroreticular strong-base resins a satisfactory analysis was possible, but again not at as low a concentration as found in most natural waters. Worth noting, however, are two points: Cr(VI) retained on strong-base resins can be displaced readily only by perchlorate; weak-base anion-exchange resins are of no use in Cr(VI) analysis.

In summation it may be stated that ion-exchange procedures can be very useful if the limitations are clearly recognized. There must be no dependence on total elution of chromium from the resin after the

trapping, which itself must be done under carefully controlled pH conditions. If speciation is attempted it should not be assumed that all anionic chromium is Cr(VI) and that Cr(III) must be cationic. The presence of complexing agents must always be considered. Certainly Florence[54], in his recent review, questions the validity of some ion-exchange speciations.

Coprecipitation

Coprecipitation procedures were developed so as to concentrate and speciate chromium in water samples. The common methods, based on selective coprecipitation of Cr(III) with iron hydroxides, are those developed by Chuecas and Riley[55] or Fukai and Vas[56]. The total chromium content may be determined after reduction so that if the initial Cr(III) content is fixed the initial Cr(VI) concentration can be determined by difference. The comparative adsorption of cationic Cr(III) and anionic Cr(VI) on the hydrated iron oxides determines how effective their separation can be.[57] Above pH 6 cationic Cr(III) is adsorbed nearly quantitatively. Anionic Cr(VI), adsorbed on the amorphous iron hydroxide at lower pH values, is carried down with the precipitate to a decreasing extent as the pH is increased. The Cr(VI) is probably adsorbed as $HCrO_4^-$ at a pH<8.5.[58] The extent of adsorption of chromium depends on the ionic environment as well as the pH. It may be enhanced by the presence of other metal ions.

Some alternative precipitation techniques have been successful for chromium[59] while other such techniques, effective for many metals, are either useless for chromium[60] or permit only partial recovery.[61] Applications of the coprecipitation techniques to solutions other than

water are comparatively rare but the iron hydroxide method has been used to remove toxic metals from waste streams.[57] An attempt at speciation of chromium in urine has even been tried.[62]

An improved iron hydroxide coprecipitation followed by ETA-AAS analysis has been reported by Cranston and Murray.[63] They determined total chromium, chromium(III) and particulate chromium in both fresh and sea water samples. A reliable analysis was claimed for the concentration range of 0.02 to 10 nM in chromium. They also seemed to have overcome the problem of background levels of chromium which are encountered in most iron sources. Although the efficiency was less than 100% this could be attributed to adsorption on container walls and filtration equipment.

Pik et al.[64] reported another variation in the procedure in that they separated the Cr(III) by the $Fe(OH)_3$ coprecipitation method but brought down the Cr(VI) with a cobalt-pyrrolidinedithiocarbamate carrier. Although the Cr(VI) precipitation was not quantitative they could still obtain reasonable results in the analysis of particulate chromium, Cr(III) and Cr(VI) by thin-film x-ray fluorescence spectrometry.

Recently the ferric hydroxide coprecipitation method for chromium concentration and speciation has come under critical scrutiny by Nakayama et al.[65,66] They found that there were problems with the coprecipitation in the presence of organic acids. It may be that a considerable proportion of the Cr(III) is so complexed in natural waters and would not coprecipitate appreciably. They devised an improved coprecipitation method[67] and classified the chromium in sea water in a

different manner: inorganic Cr(III), organic Cr(III), and Cr(VI). Their findings would dictate that all reports on chromium speciation prior to the 1980's require re-examination. Any analysis based on stored samples is suspect, particularly if stored under acidic conditions. Cr(VI) would be reduced and any organic Cr(III) dissociated so that the results would be highly biased toward inorganic Cr(III). Even with prompt analysis there could be problems. The values reported for Cr(VI) probably include organic Cr(III) as well, since it is unlikely to precipitate with the inorganic Cr(III).

Solvent Extraction

Most solvent extraction procedures used in examining the chromium species in aqueous solutions depend upon the extraction of Cr(VI). Ammonium pyrrolidine dithiocarbamate (APDC) - methyl isobutyl ketone (MIBK) extractions are favoured by a number of scientists.[68,69,70] Amine extractions, such as those reported by de Jong and Brinkman[71], have shown some success. De Jong and Brinkman[71] suggest that extractions by APDC or by diethyldithiocarbamate are too dependent on the water sample to be successful - extractions of Cr(VI) vary from 50 to 100%. They also discount the coprecipitation methods because Cr(VI) is partly adsorbed on the precipitate. Their amine extraction, involving the combined use of thiocyanate and oxidation methods, made it possible to differentiate between the several forms of chromium present in natural waters.

Generally, solvent extraction methods have not been applied in chromium analysis of biological materials but they are gaining greater acceptance for systems other than just water. Tanaka and Ishimaru[72]

have analyzed sludge and sediment making use of a trioctylamine-benzene extraction.

Recently there have been some studies in which the different speciation/concentration methods have been used with the same samples. Osaki et al.[73] determined chromium in natural waters by means of solvent extraction with APDC into chloroform and by coprecipitation with Fe(III) hydroxide. In the comparison the effects of organic matter and colloidal particles were recognized. Neither method was always quantitative - the degree of coprecipitation of Cr(III) ranged from 87% to 100%; the extraction of Cr(VI) was incomplete. Nevertheless, acceptable results were obtained with both approaches. The separation of Cr(III) from Cr(VI) by the solvent extraction method was more effective; there was little transfer of Cr(III) in any form to the organic phase. Apparently a Cr(III) species which contributed to error in the Cr(VI) analysis could not be identified. The authors conclude that unless this was known "it is difficult to rule out the possibility of a large error in the determination of Cr(VI)".

In such an examination of the contending separation procedures it becomes apparent that ion-exchange and coprecipitation methods have at least as many problems associated with their use in chromium speciation as do liquid-liquid extraction methods, yet they are in practical terms not as easily performed. It was decided that an extraction method would best meet the objectives of this research program. Among the potential extractants is diphenyl-2-pyridylmethane (DPPM). While it has been reported as being very selective for Cr(VI) there are a number of aspects associated with its use which have not

been examined.[74] Certainly no analytical procedure involving DPPM has been reported. However, in any developmental work not only must the extraction system be investigated but also there must be an examination of the nature and reactions of chromium at trace concentrations in aqueous solutions.

Most scientific problems are far better understood by studying their history than their logic.

Ernst Mayr

2. THEORY AND BACKGROUND

2.1 Chromium in Solution

Most people drink about 2 L of water per day. Although the food consumed is the main source of the essential trace chromium there can be chromium in the water. How much chromium does the water intake represent? Is the micronutrient at a high enough level in solution to have a nutritional effect or is it in a form which could be a health hazard? The Guidelines for Canadian Drinking Water Quality reads[75]:

> **Chromium:** A maximum acceptable concentration for chromium in drinking water of *0.05 mg/L* has been established on the basis of health considerations. Trivalent chromium, the most common naturally occurring state of chromium, is not considered to be toxic; however, if present in raw water it may be oxidized to hexavalent chromium during chlorination. Toxic effects of chromium in man are attributed primarily to this hexavalent form. At the maximum acceptable concentration in drinking water, hexavalent chromium has not resulted in any known harmful effects on the health of man or animals. The objective concentration is *less than or equal to 0.0002 mg/L.*

Fortunately, the concentration of chromium is low enough in Canadian drinking waters[19] that there need be little concern. However, Angino et al.[76] have expressed some concern about the higher than acceptable levels in some American supplies and about the poorly designed studies and poorly generated data available.

Another concern is the impact of industrially generated chromium on the world's ecosystem. Galloway[77] estimates that the global injection of chromium into the environment is:

Industrial/municipal waste water = 55×10^3 tonnes/year

Combustion (atmospheric release) = 1.5×10^3 "

Natural weathering = 50×10^3 "

The impact of waste water on the geological cycle can be significant and, it must be remembered, much of the chromium from industrial sources originates as Cr(VI). Further, although most elements such as chromium end up in the sediments[78] the removal mechanism is not well understood.[79,80,81] Before this removal what is the form and environmental effect of this chromium?

Speciation in Natural Waters

It becomes obvious that to understand the effect of chromium in any situation the forms of the element in solution as well as the concentration must be examined. A theoretical approach, based on the known chemistry of chromium, may be of value in explaining the analytical data available, incomplete though it may be. If any valid results concerning speciation are expected the effects of the conditions employed during the analysis must be taken into account.

In the absence of both inorganic and organic complexing agents, thermodynamic considerations dictate that in natural waters the Cr(VI) would occur as an anionic species while the Cr(III) could be present as either cationic or anionic species, depending upon the pH. Using information available in the Atlas of Electrochemical Equilibria in

Aqueous Solutions[82] the proportion of each form of chromium has been calculated at different acidities. These results are represented in Figure 2.1a and 2.1b, where each appropriately hydrated form is related to Cr^{3+} - for Cr(III) - and CrO_4^{2-} - for Cr(VI) - respectively. Since dichromates cannot exist to any significant extent at trace levels they are not included in these figures.

A paper which has appeared subsequent to these calculations does support this approach. Tandon et al.[83] have calculated the % of each Cr(VI) species in aqueous solutions at various total Cr(VI) concentrations and pH values from 1 to 8. While depicted differently, their results are equivalent to those depicted in Figure 2.1b.

These figures are of particular value when the form of chromium is important to the understanding of a system. For instance, the forms which predominate at any pH may determine the effectiveness of a separation scheme.

In air saturated solutions it should be possible to calculate which of the oxidation states, Cr(III) or Cr(VI), is prevalent, if valid thermodynamic data are available. In most reports it is accepted that Cr(VI) should prevail[66,84,85,86] but there are instances where it is stated that Cr(III) is favoured according to the thermodynamic considerations.[18,55] Of the several reports the one by Elderfield[84] is most easily followed wherein he shows that Cr(VI) should prevail in ocean water; $\log[Cr(VI)]/[Cr(III)] = 21.1$ at pH 8.1.

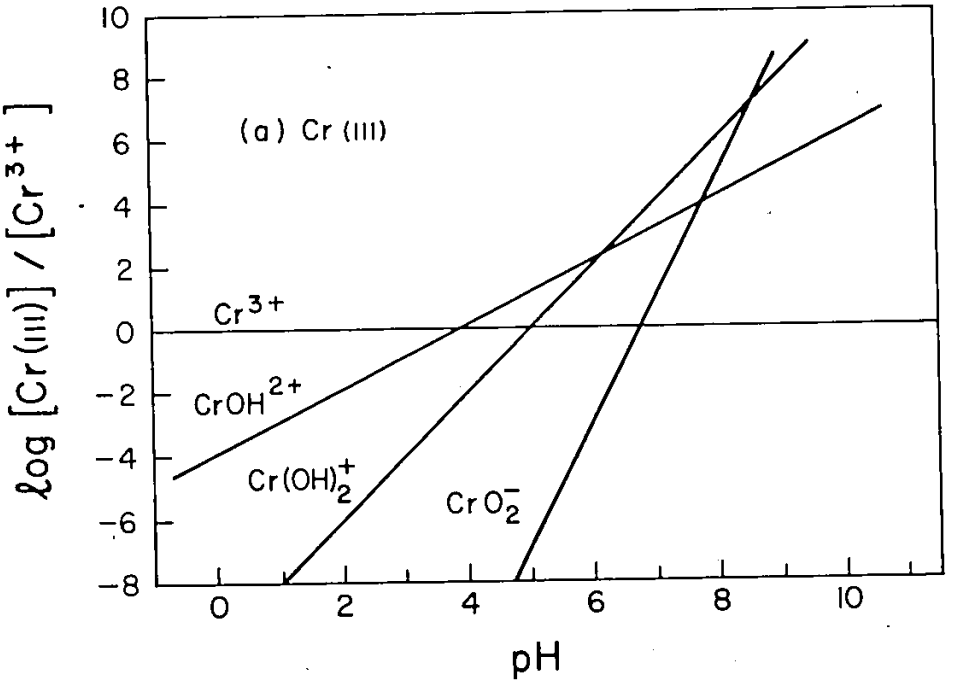
By employing a similar approach to that of Elderfield[84] the calculation of the chromium speciation by oxidation state was undertaken

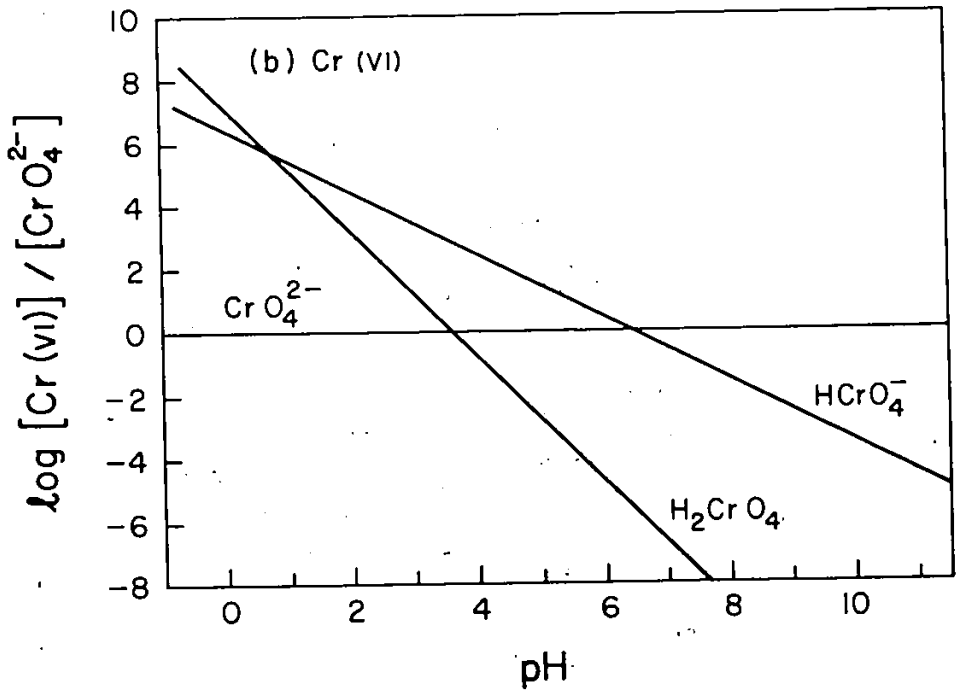
Figure 2.1

(a) Cr(III). Distribution of Cr(III) complexes as a function of pH. The logarithm of the ratio of the concentration of $CrOH^{2+}$, $Cr(OH)_2^{+}$ and CrO_2^{-} to that of Cr^{3+} is represented.

(b) Cr(VI). Distribution of Cr(VI) complexes as a function of pH. The logarithm of the ratio of the concentration of $HCrO_4^{-}$ and H_2CrO_4 to that of CrO_4^{2-} is represented.

Note: The figures are based on calculations performed using the equations and data from the Atlas of Electrochemical Equilibria in Aqueous Solutions[82].


(a) Cr (III)
log [Cr (III)] / [Cr3+]
Cr3+
CrOH2+
Cr(OH)2+
CrO2−
pH


(b) Cr (VI)
log [Cr (VI)] / [CrO4 2−]
CrO4 2−
HCrO4−
H2CrO4
pH

for acidic solutions. The known redox conditions for air saturated water[66,84]

$$pH + pE = 20.6 \qquad (2.1)$$

and the redox equations listed by Pourbaix[82] were used. Only the uncomplexed dominant species were considered under equilibrium conditions in each pH range. Selected results are represented in Figure 2.2; the solid line represents the domain of importance of a particular Cr(VI)/Cr(III) pair and the dashed line indicates a diminishing significance.

Except under quite acidic conditions the dominant oxidation state should be Cr(VI). However, the common practice of stabilizing water samples by adding HNO_3 would be expected to promote the conversion of Cr(VI) to Cr(III). This may be one reason why many of the earlier attempts at speciation gave such variable results but ones which suggested that Cr(III) predominated in natural waters.

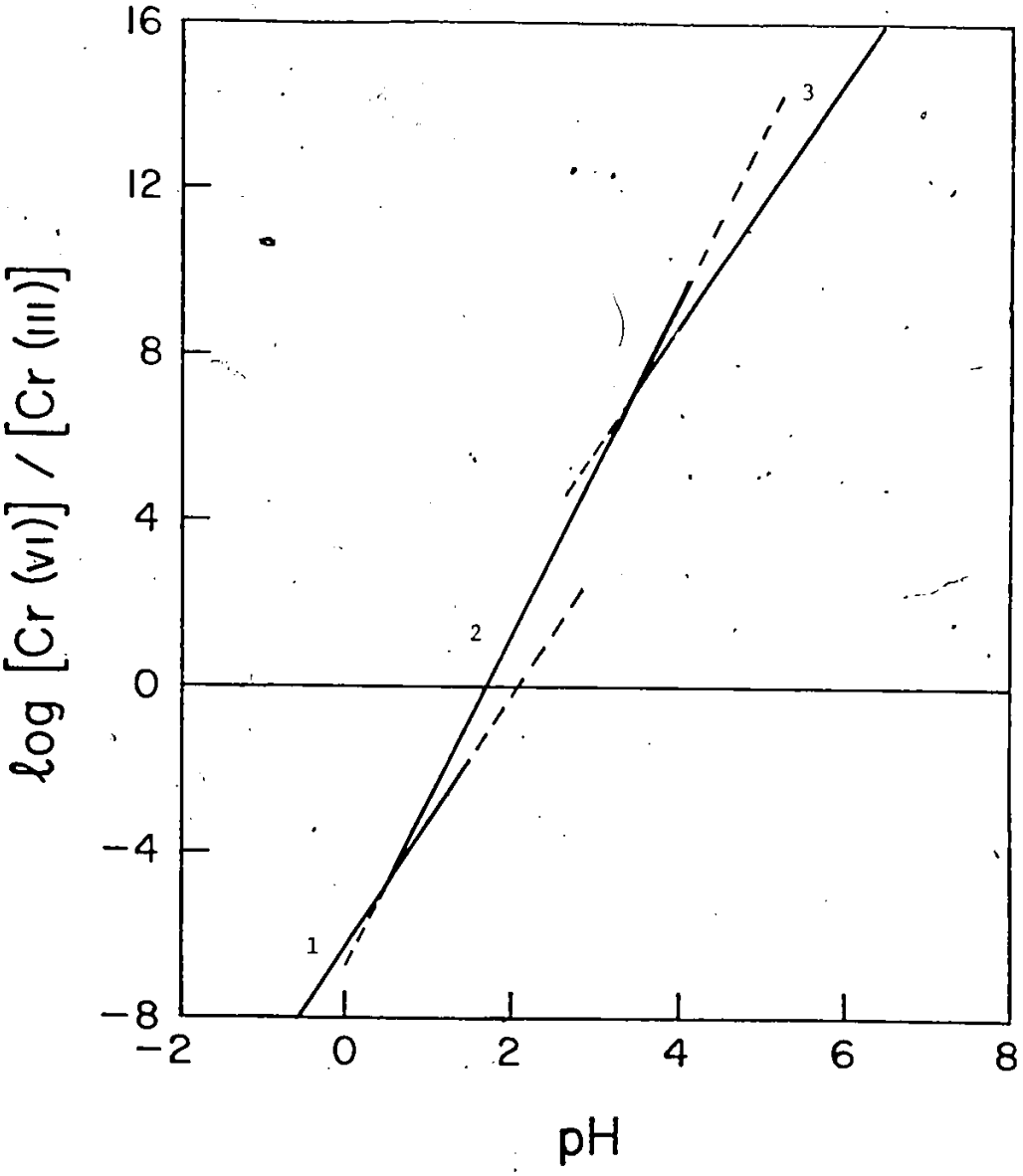
Although Cr(III) should definitely be oxidized in air saturated solutions above pH 3 the oxidation does not generally proceed quickly.[85] The extent of any oxidation may not be measurable in the short run. Therefore, it may be that kinetics play an important part in chromium speciation, potentially as much as the thermodynamic equilibrium considerations in some situations. However, Hoffmann[87] expresses a concern about this situation. He suggests that the kinetically hindered reactions could be sensitive to trace metal catalysis so that the notion of safe disposal of Cr(III) to aquatic systems must be examined in the light of potential catalytic conversion to toxic Cr(VI).

Figure 2.2

Chromium specaition by type and oxidation state as a function of the pH for those complexes prevailing at trace concentrations in acidic oxygenated solutions.

1. $\log [H_2CrO_4]/[Cr^{3+}]$
2. $\log [HCrO_4^-]/[Cr^{3+}]$
3. $\log [HCrO_4^-]/[CrOH^{2+}]$

Note: The figure is based on calculations performed using the equations and data from the Atlas of Electrochemical Equilibria in Aqueous Solutions[82] and does not reflect the type of acid controlling the pH of the air saturated solutions. Despite such limitations it is clear that the lower oxidation state should prevail only in quite acidic solutions.


16
12
8
4
0
−4
−8
−2
0
2
4
6
8
log [Cr (VI)] / [Cr (III)]
pH
1
2
3

When dealing with chromium in natural waters at trace levels the chromium may be present as simple aquated ions or as metal-inorganic ion complexes and metal-organic complexes. The formation of these complexes of chromium cannot be dealt with easily. Although the stability constants and profiles for a number of Cr(III) complexes are available[85], in the formation of the complexes it is necessary to consider the inertness of the chromium polyhydroxides and the slowness of Cr(III)-ligand reactions. Further, in real systems, even if equilibrium conditions can be assumed to prevail, there is no single complexing agent, and for those complexing agents thought to be most important there is little thermodynamic data.

Varshal et al.[88] examined the interactions of metal ions with organic matter in surface waters and found that organic ligands, particularly from fulvic and humic acids, dominate the coordination forms for minor elements. Van den Berg van Saparoea[89] found that in the water samples in southern Ontario there was a surplus of complexing ligands present. In dystrophic waters, of low pH and ionic strength, there was a particularly high concentration of fulvic acid-type ligands. The effect of such naturally occurring organic materials on the complex formation of Cr(III) is now of interest and has been investigated by Nakayama et al.[65] and Yamazaki et al.[90]

These humic substances are important components in the organic geochemical cycle and in the chelation of trace metals of biologial importance not only in the aquatic environment but in sediments and soils as well. The organometal ion complex(es) must be quite stable. Guy and Chakrabarti[91] claim that metal ions are in a bound form at a pH

as low as 3. Wilson et al.[92] have recently examined the structure of fresh water humic materials so as to clarify the nature of their binding sites. While such substances are more complex, it could be that a simple organic acid such as oxalic acid, for which there is a wealth of information[85], would serve as a model in the Cr(III)-complex formation. At a pH lower than 5 it is known that phenolic materials may be oxidized to oxalic acid and at a low pH many other organic acids behave in a manner similar to oxalic acid.[91] Slavek et al.[93] have found that in treated soil samples, when they were looking at the selective extraction of metal ions associated with humic acid, a major product was oxalic acid. It can be concluded that Cr(III) may often be complexed with organic ligands in the environment. While there is no completely satisfactory model for this complexing phenomenon it may be possible to use a simple substance such as oxalic acid to examine the reactions.

Trivalent chromium may form a large number of complexes with inorganic anions as well as the organic substances found in natural waters. However, Elderfield[84] has shown that ion-pairs between Cr(III) and Cl^-, Br^-, SO_4^{2-}, HCO_3^-, CO_3^{2-} etc. are insignificant. Even mixed complexes involving hydroxide ions as well as these anions will be low in concentration in natural waters. Most complexes should involve the hydroxide ion alone. For example, in sea water at pH 8.1, he suggests that the Cr(III) species, if present, should be $Cr(H_2O)_4(OH)_2^+ \simeq 85\%$, $CrO_2^- \simeq 13.5\%$, with $Cr(H_2O)_5OH^{2+}$ and any mixed complexes making up the balance, in the absence of organic complexing agents. This would be in substantial agreement with the analysis illustrated in Figure 2.1. Florence and Batley[94] have considered such complexing as well. They

depict such species in a figure representing chromium in natural waters but do not attempt to assign proportions to each possible form.

Further, Florence and Batley[94] examined the valency-state distribution of dissolved chromium. They decided that this will depend upon:

1) The oxygen content and redox potential
2) The presence of dissolved or particular organic matter
3) The presence of suspended inorganic matter

However, these are not mutually independent factors. For instance, Nakayama et al.[66] point out that Cr(III) is easily oxidized to Cr(VI) in the presence of manganese oxides and at the same time organic material can reduce the Cr(VI) in natural sea waters. Cranston[95] has found that the concentration and speciation of chromium vary with both location and depth in ocean waters. The Cr(III) formed by reduction of Cr(VI) in deep anoxic waters is thought to diffuse into the overlying oxygenated water and is transformed by oxidation to Cr(VI) or removed by adsorption onto particulate matter. The Cr(III) content also appears to be related to biological activity.

As far as Cr(VI) is concerned, it is not expected to be complexed in natural waters. Although it is unlikely to be bound to organic matter or adsorbed on colloidal particles, the presence of such substances can influence the Cr(VI) concentration, or its determination by analytical methods.

As mentioned, the oxidation state of chromium in soils as well as waters is controlled by in situ redox processes. Amacher[96] has shown that the immediate availability of chromium in soils is probably

controlled through oxidation by manganese oxides while long term control is probably exerted through reduction by organic matter. Fulvic acid reduces Cr(VI) slowly in soil but once reduced the chromium is bound to organic matter or sorbed to iron oxides. This means that in any watershed the chromium content and speciation may be influenced by previous contact with ground matter.

In summation, in natural waters if redox considerations alone are of importance then Cr(VI) should be the predominant species. Even if the Cr(VI) is reduced the majority of the Cr(III) species should be sorbed onto particulates to be eventually incorporated into the sediment, as is the ultimate fate of most heavy-metal ions.[78,90] However, if as recently suggested[65,73,90] the Cr(III) can exist as soluble anionic or uncharged species, probably associated with organic complexing agents, then much of the soluble chromium need not be as Cr(VI) alone.

Experimentally this speciation question has not been resolved. It would be expected that different waters could have not only a different chromium content but also different proportions of each oxidation state. However, even for ocean waters supposedly at equilibrium the experimental values are not agreed upon. While the total chromium content may be determined by modern instrumental methods, recognized as about 0.3 ppb[73], each speciation report seems to yield a different value for the relative oxidation state. This Cr(VI)/Cr(total) ratio is reported in the literature with a range of from 0.0 to 0.98; ie. from no Cr(VI) to almost all Cr(VI).[94].

The Effect of Acids on Cr(VI)

Before speciation a separation process must be employed. This can cause changes in the form of chromium present in the original aqueous solution. The consequences that arise for both Cr(VI) and Cr(III) when there is a change in pH must be considered as well. While the effects of pH have been mentioned, as have the effects of complexing agents on Cr(III), an additional examination is required for Cr(VI). The equilibria of Cr(VI) species, particularly in acid solutions with various anions, must be considered before a separation by an extractant such as DPPM can be appreciated.

Equilibria prevailing in acid aqueous Cr(VI) solutions have been studied most often by spectrophotometric methods. A few of the most pertinent reports should be examined.[97-106]

Cr(VI) exhibits various equilibria, some of which are very concentration dependent. For instance, dichromates are of importance only when the total Cr(VI) concentration exceeds about 4×10^{-4} M.[97,98] In the absence of interactions of anions the following equations are applicable (the equilibrium constants are listed below the appropriate equation without the units) :

$$H_2CrO_4 \rightleftharpoons HCrO_4^- + H^+ \qquad (2.2)$$

$K' = 0.18$[102], 1.21[99], 4.16[101a], $4.5\text{-}6.5$[98], 6.3[97]

The most recent value of K = 6.3 at an ionic strength μ = one, obtained by Lukkari[97], was used in any subsequent calculations.

$$HCrO_4^- \rightleftharpoons CrO_4^{2-} + H^+ \qquad (2.3)$$

$K = 3.2 \times 10^{-7}$ [102]

$$2HCrO_4^- \rightleftharpoons Cr_2O_7^{2-} + H_2O \qquad (2.4)$$

$K = 98^{99}, 97.5^{97}$

$$HCr_2O_7^- \rightleftharpoons Cr_2O_7^{2-} + H^+ \qquad (2.5)$$

$K = 0.85^{99}$

$$H_2Cr_2O_7 \rightleftharpoons HCr_2O_7^- + H^+ \qquad (2.6)$$

$K \approx 10^{8}$

All such equilibria have been involved in the construction of Figure 2.1b since Pourbaix's Atlas of Electrochemical Equilibria in Aqueous Solutions[82] contains but an alternative representations of such information.

In the presence of HCl additional equilibria apply since Cr(VI) does undergo reactions in such a system.

$$HCrO_4^- + HCl \rightleftharpoons CrO_3Cl^- + H_2O \qquad (2.7)$$

$K = 1.1 \times 10^{5}$ [100], 17 ± 2[98], 10.7 ± 0.07[97], 11[101b]

Again the value of K = 10.7 reported by Lukkari[97] seems to be the most appropriate to adopt in any calculations. The evaluation was done with the previous reports in mind. The extreme difference in the value reported by Cohen and Westheimer[100] could be explained as being due to their acetic acid medium used in its determination. Haight et al.[98] reported the value which is within an acceptable range for such determinations and considered an additional reaction:

$$H_2CrO_4 + Cl^- \rightleftharpoons CrO_3Cl^- + H_2O \qquad (2.8)$$

$K = 105 \pm 20$[98]

Haight et al.[98] also examined the reactions of Cr(VI) in the presence of other acids and concluded that the mononuclear species of Cr(VI) present in dilute solutions are:

$HCrO_4^-$ in acetic acid

$HCrO_4^-$ and H_2CrO_4 in perchloric acid and nitric acid

$CrSO_7^{2-}$ in sulfuric acid produced by the reaction

$$HCrO_4^- + HSO_4^- \rightleftharpoons CrSO_7^{2-} + H_2O \qquad (2.9)$$

$K = 4.1$ [98]

The thiosulfatochromium(VI) ion has been proposed as well[104,105] but it is thought to be sulfur bonded and has a much higher equilibrium constant than the species bound to chromium via oxygen bonds.

One other important inorganic acid thought to react with Cr(VI) is phosphoric acid. Halloway[103] proposed the reaction:

$$HCrO_4^- + H_3PO_4 \rightleftharpoons H_2CrPO_7^- + H_2O \qquad (2.10)$$

$K = 9.4$ [103]

$$HCrO_4^- + H_2PO_4^- \rightleftharpoons HCrPO_7^{2-} + H_2O \qquad (2.11)$$

$K = 2.9$ [103]

A general mechanism for all such substitutions on the tetrahedral hydrogen chromate ion in acidic aqueous solutions has been proposed by Lin and Beattie.[106]

Since the Cr(VI) species present in an acidic solution can differ in the presence of different anions the possible equilibrium forms must be considered in any instance where Cr(VI) is being used as an oxidizing agent. The form as well as the concentration and pH of the oxidizing agent can be of importance. It has been shown that the rate of an oxidation reaction involving chromic acid diminishes in the

presence of Cl^- [100]. It is assumed that there is a competition between the oxidation reaction and the formation of the chlorochromate ion. The chlorochromic acid then present is a less efficient oxidizing agent than the acid chromate ion.[107]

Lee and Stewart[108] examined the nature of Cr(VI) in acid solutions and its relation to alcohol oxidation. They found that protonation of the acid chromate ion is accompanied by incorporation of the mineral acid anion into the Cr(VI) species.

$$HCrO_4^- + 2H^+ + A^- \rightleftharpoons HCrO_3A + H_2O \qquad (2.12)$$

They interpreted the spectral evidence and the results for the oxidation experiments to suggest that CrO_3A^- is not present in significant concentrations under conditions where the monoanion is the dominant species but that $HCrO_3A$ is the major neutral species.

$$H_2O + CrO_3A^- \rightleftharpoons HCrO_4^- + HA \qquad (2.13)$$

$$H_2O + HCrO_3A \rightleftharpoons H_2CrO_4 + HA \qquad (2.14)$$

ie. the equilibrium represented in (2.13) would seem to be to the right but the equilibrium represented in (2.14) to the left. They proposed the Cr(VI) mineral acid species illustrated previously but, in contrast to Haight et al.[98], suggested also that perchloric acid and nitric acid could form such complexes. The pKa value of chromic acid in aqueous solutions of the different mineral acids varied. This was in the same order as the oxidizing ability of the protonated species $HCrO_3A$: $H_3CrPO_7 < HCrClO_3 < H_2CrSO_7 < HCrClO_7 < HCrNO_6$.

While chromates are readily reduced in acid solutions containing reducing agents the reduction to Cr(III) can occur in concentrated acids alone. Lukkari[97] has examined this reduction in Cr(VI) solutions of

greater than 4×10^{-4}M in the presence of 1-6M HCl and 1-7M $HClO_4$. The magnitudes and rates of the change from Cr(VI) to Cr(III) vary inversely as the total Cr(VI) concentration and directly as the acid concentration. By comparing the HCl and $HClO_4$ acid systems it could be concluded that both hydrogen and chloride ions accelerate the reduction. These results were qualitative only, based on the observed changes in the spectra with time.

Lukkari[97] also found that ordinary daylight promoted the reduction of Cr(VI). This effect of light, in the somewhat different photochemical oxidation of alcohols by potassium dichromate, has been reported by Bowen et al.[109,110] in the 1930's. They attributed all of the photoactivity to the $HCrO_4^-$ ion and proposed a mechanism involving this species. Milyawa et al.[111] examined the reduction of bichromate ions in a hydrochloric acid medium. They also found that light had an effect on the rate of reaction by following the liberation of chlorine. From this information it should be suggested that CrO_3Cl^- may be photoactive.

While the reduction of Cr(VI) at high acidities could be predicted thermodynamically the inverse relationship for the magnitude and rate of change with [Cr(VI)] has not been widely recognized. It does not follow that this information is of any importance when dealing with trace levels of chromium at the much higher pH values of natural waters but one should be aware that such reductions are possible. Certainly, in any speciation technique involving an acidic solution the reduction of Cr(VI) must be of concern.

The equilibrium distribution of Cr(VI) species in the presence

of various acids may be calculated using the equations and equilibrium constants which have been listed. To illustrate how the concentration of the acid can influence the proportion of each species the situation will be examined for hydrochloric acid. This is of particular interest because Cr(VI) can be extracted from this acid by DPPM.

In the presence of HCl there should be no CrO_4^{2-} ions (equation 2.3). Further, at trace levels there need be no dichromate complexes considered. To determine the type and proportion of possible Cr(VI) species one additional equilibrium equation must be written:

$$CrO_3Cl^- + H^+ \rightleftharpoons HCrO_3Cl \qquad (2.15)$$

This represents the reverse of the acid dissociation of $HCrO_3Cl$. Unfortunately, the value of Ka for this acid is not available in the literature. It has been suggested that it should be of similar acid strength as H_2CrO_4, possibly stronger.[100]

Using the equilibrium constants listed by Lukkari[97] for equations (2.2) and (2.7) it is possible to calculate the proportions of the major species present in a trace Cr(VI)-HCl solution if certain values can be assumed for the equilibrium constant of equation (2.15). Data from such calculations are represented in Table 2.1. At the various HCl concentrations the first value listed is the fraction of the components present if the formation of $HCrO_3Cl$ is neglected ($Ka_{15} = \infty$), the second value is for $Ka_{15} = 10$ and the third value is for $Ka_{15} = 5$.

It can be seen from Table 2.1 that if the formation of $HCrO_3Cl$ is neglected there is a gradual and continuing increase in the proportion of CrO_3Cl^- present, formed primarily at the expense of $HCrO_4^-$, as the HCl concentration is increased. On the other hand, if

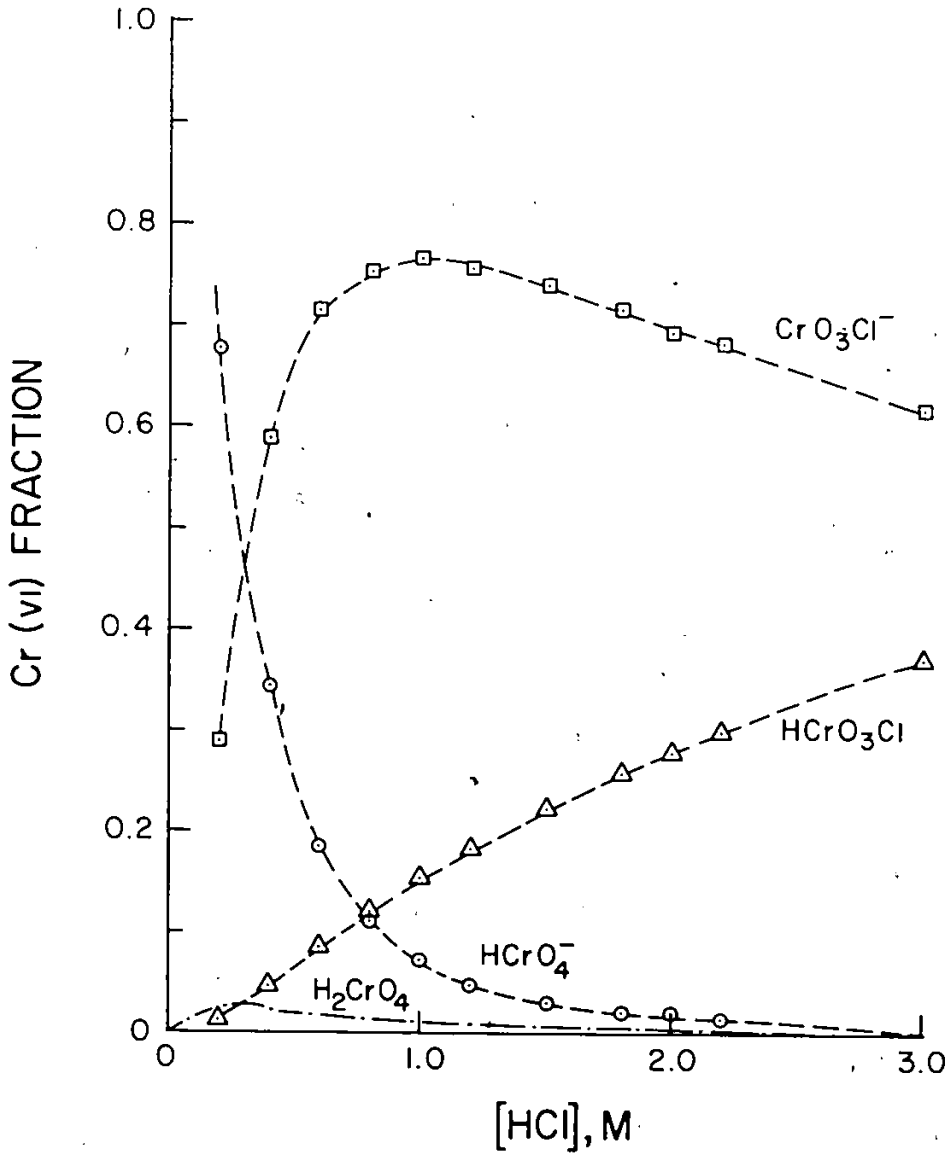
TABLE 2.1

Proportions of Cr(VI) in several forms as a function of the concentration of hydrochloric acid.

HCl (M)	Ka	H_2CrO_4	$HCrO_4^-$	CrO_3Cl^-	$HCrO_3Cl$
0.2	∞	0.0217	0.685	0.293	0.0
	10	0.0216	0.681	0.292	0.0058
	5	0.0215	0.677	0.290	0.0116
0.4	∞	0.0229	0.360	0.617	0.0
	10	0.0223	0.352	0.602	0.0241
	5	0.0218	0.343	0.588	0.0470
0.6	∞	0.0193	0.202	0.779	0.0
	10	0.0184	0.193	0.744	0.0446
	5	0.0176	0.185	0.712	0.0854
0.8	∞	0.0159	0.125	0.859	0.0
	10	0.0149	0.117	0.803	0.064
	5	0.0140	0.110	0.755	0.121
1.0	∞	0.0134	0.0846	0.905	0.0
	10	0.0123	0.0774	0.828	0.0828
	5	0.0113	0.0714	0.764	0.153
1.2	∞	0.0115	0.0603	0.928	0.0
	10	0.0103	0.0542	0.835	0.100
	5	0.0094	0.0493	0.759	0.182
1.5	∞	0.0094	0.0395	0.951	0.0
	10	0.0082	0.0346	0.832	0.125
	5	0.0073	0.0307	0.740	0.222
2.0	∞	0.0072	0.0227	0.970	0.0
	10	0.0060	0.0190	0.812	0.162
	5	0.0052	0.0163	0.699	0.280
3.0	∞	0.0049	0.0102	0.985	0.0
	10	0.0038	0.0079	0.760	0.228
	5	0.0031	0.0064	0.619	0.371

Figure 2.3

The proportion of each Cr(VI) complex at trace concentrations in an aqueous hydrochloric acid solution as a function of the acid concentration. This representation is based on calculations using a dissociation constant for $HCrO_3Cl$ as Ka = 5 (Table 2.1).


1.0
0.8
0.6
0.4
0.2
0
Cr (VI) FRACTION
CrO_3Cl^-
$HCrO_3Cl$
$HCrO_4^-$
H_2CrO_4
0
1.0
2.0
3.0
[HCl], M

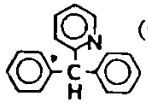
the formation of $HCrO_3Cl$ is considered then the production of this acid competes with the production of CrO_3Cl^-. Even though the amount of $HCrO_4^-$ present has a more rapid decrease the proportion of CrO_3Cl^- is never as great at a chosen HCl concentration. The proportion of CrO_3Cl^- present maximizes then slowly declines as the HCl concentration increases. A graphic representation of this phenomenon is illustrated in Figure 2.3, where the proportion of each component is indicated as a function of the HCl concentration, using Ka = 5.

The form of Cr(VI) in aqueous acidic solutions could be estimated for the other acids as well as for the HCl solutions. However, it is sufficient to recognize that the nature of the Cr(VI) species in the aqueous phase may determine the complex extracted and the distribution ratio in any solvent extraction procedure. It could also account for the significant acid (anión) dependence sometimes observed in some extractions; ie. extraction of certain complexes of Cr(VI) may be favoured while other forms may extract only poorly. As will be seen, there is considerable controversy in the literature concerning the Cr(VI) complex extracted in some systems.

2.2 Solvent Extraction

In this thesis there is a limited explanation of the theoretical aspects of the solvent extraction process and a selected review of the available literature. Sekine and Hasegawa[112] may be consulted for a more complete treatment and for over 7000 literature references. Although solvent extraction methods are becoming more important

industrially, particularly in mining and metallurgy, this is not the focus of the investigation. Again, reviews with this perspective are available.[113,114,115,116] The focus of this thesis will be upon those aspects which seem pertinent to the extraction of aqueous acids and anionic metal complexes by diphenyl-2-pyridylmethane (DPPM) in selected organic diluents.

The application of DPPM, a substituted pyridine with the structure  (molar mass 245.33), in solvent extraction processes may be regarded as analogous to that of the tertiary amines. Reviews of the extraction by tertiary amines may be found in the literature.[117,118]

Essential to an understanding of how the pyridinium salt may be effectively formed and extracted to the organic phase is some knowledge about the potential for protonation of DPPM. According to Brown and Mihm[119] the ionization constant for pyridines substituted at the 2-position decreases with increasing substituent size. In their review, Clark and Perrin[120] developed the equation

$$pKa = 5.25 - 5.90\ \Sigma\sigma \qquad (2.16)$$

to predict the base strength of substituted pyridines, where σ is a parameter representing combinad effects primarily of resonance and inductive types. While the pKa for DPPM cannot be calculated, because the appropriate σ value is not available, it should be lower than for that of the single phenyl substituent ($\sigma = 0.02$) and in keeping with the value of pKa = 4.41 reported by Ejaz et al.[121]

Clark and Perrin[120] point out a further important consideration which could be of significance in this research - the solvation effects.

Solvation can be important in stabilizing a cation in aqueous solution, both by suitable orientation of water molecules around the basic centre and by hydrogen bonding of the type, $\geq N^{+}H...OH_2$, between water and the hydrogen atom attached to the basic centre. This stabilization will vary with the available space around the basic centre and would be less for pyridine, especially as substituted in DPPM, than for most other N containing basic extractants.

Thus, DPPM is a rather large but very weak base, certainly weaker than the tertiary amines commonly used in solvent extraction systems and weaker than other substituted pyridines examined by Ejaz et al.[122] The decreased base strength may favour the selectivity of DPPM for Cr(VI) just as the weaker tertiary amines are more selective extractants than their secondary amine counterparts. Steric considerations may be as important a factor as base strengths but, despite extensive studies, a theoretical explanation of the variation of any distribution constant with the degree or type of substitution has not so far been possible.[123] The overall effect is the result of numerous factors which influence the chemical and electrostatic interactions in the system as a whole.

Fundamentals

In outlining some of the fundamentals of liquid-liquid (solvent) extraction chemistry one appropriate approach parallels that of Minczewski et al.[123]; particularly since the ultimate concern is the separation and preconcentration of a trace inorganic species. The following interpretation, based in part on their theoretical development, documented by nearly 1400 references, and on the

information in the book by Sekine and Hasegawa[112], is directed to encompass the specific concern of this thesis.

In extraction, where a chemical species is transferred from an aqueous to an immiscible organic solvent, the concentrations (strictly the chemical activities) of the solute in the two phases are mutually related. This equilibrium at a given temperature, provided that the solute is the same species in each phase, may be expressed as a distribution constant:

$$K_d = \bar{C}/C \qquad (2.17)$$

where C is the concentration of the solute. The convention of using a "bar over" notation for the organic phase, leaving the aqueous phase unabridged, has been adopted. While at high concentrations the simple distribution law may not be followed, for those extractions at trace concentrations the distribution constant is independent of the solute concentration because the activity coefficient is equal to unity in both phases.

A more useful parameter is the distribution ratio (coefficient) D. Since K_d can be determined readily only if the solute remains as a single species and is identical in both phases, it is more practical to determine the total concentration of a species, [A], irrespective of its form, in the organic and aqueous phases at equilibrium.

$$D = \Sigma\bar{C}_A/\Sigma C_A = [\bar{A}]/[A] \qquad (2.18)$$

In practice a quantity referred to as the percentage extraction, %E, is used to express the extraction efficiency. If the masses of species, A_m, in all possible forms in each phase are known:

$$\%E = 100\Sigma\bar{A}_m/(\Sigma A_m + \Sigma \bar{A}_m) \qquad (2.19)$$

It is more likely that the concentration of the species, [A], in a volume, V, of each phase is determined. Then

$$\%E = \frac{100\bar{V}[\bar{A}]}{\bar{V}[\bar{A}] + V[A]} \qquad (2.20)$$

Although this approach is common, particularly in industrial applications, it is simply a choice, perceived as a convenience, because the percentage extraction and the distribution ratio can be related easily:

$$\%E = 100D/[D + V/\bar{V}] \qquad (2.21)$$

Whereas the distribution ratio remains relatively constant when the extraction ratio, $V/\bar{V}$, changes, the %E shows a marked variation. When the objective of an extraction is the preconcentration of a trace element great care must be taken to ensure that the effect of increasing the extraction ratio, in an attempt to increase the analyte concentration in the organic phase, is understood clearly. Cresser[124], in describing the uses of solvent extraction in flame spectroscopic analysis, illustrates these relationships between the percent extraction, the distribution ratio and the extraction ratio in a useful form.

Although not always employed, another parameter which is called the enrichment factor, F, has been used in this investigation. It is the ratio of the concentration of the analyte in the organic phase after extraction to the concentration of the analyte in the original aqueous solution. Recently Mizuike[180] has defined this parameter in the symbolic fashion

$$F = \frac{Q_T/Q_M}{Q^\circ_T/Q^\circ_M} = \frac{R_T}{R_M}$$

where Q°_T and Q_T are the quantities of the desired trace element before and after the enrichment, respectively; Q°_M and Q_M

are the quantities of the matrix before and after the enrichment, respectively; R_T is the trace recovery; R_M is the yield of the matrix. However, when applied to solvent extraction systems a modification of this symbolism seems in order. F may be easy to measure and can be related to the other parameter by the equations:

$$F = (\%E/100)(V/\bar{V})$$

$$= \frac{D}{D + V/\bar{V}} (V/\bar{V}) \qquad (2.23)$$

The general applications of this F parameter are mentioned below and further illustrated in Appendix A, where specific cases relating to the research on chromium extraction are exemplified.

The F parameter can be useful when designing an extraction experiment. It may be used to determine whether or not an analyte can be enriched by an extraction sufficiently to be detected by a particular analytical method. Then the extraction ratio for a chosen system may be optimized (Appendix A1).

In a practical sense, single batch extractions in which a large % of the analyte is recovered in the organic phase are preferable to the multiple extractions sometimes required to remove the same proportion of analyte from the original solution. This is particularly true when out of the laboratory sampling is required. Obviously, the higher the value of D the more easily any desired recovery objective can be met (Appendix A1).

The separation of a metal analyte from the bulk matrix and other metals in the solution may be as important as the requirement of enrichment. On occasions the analytical technique employed is not

limited because it cannot detect the analyte at the concentration present but because there are interferences caused by other substances in the solution. The extent to which such a selective separation is possible may be determined if the values of D for extractable species are known. The separation of two metallic species is commonly described in terms of the separation factor α.

$$\alpha_{1,2} = D_1/D_2 \qquad (2.24)$$

However, it is not only this ratio but also the absolute values of each D which determines the effectiveness of any separation. Again, the F parameter can be of considerable value in determining quickly the conditions necessary for the effective separation (Appendix A2).

It is clear that to meet the objectives of enrichment or separation of an analyte may require a difference in approach. However, on occasions both objectives must be met simultaneously. The analyte of interest could be at too low a concentration to be determined by a given procedure yet a simple enrichment may not satisfactorily remove an interfering species. A solvent extraction enrichment followed by scrubbing may overcome the difficulty. The scrubbing process involves the mixing of the organic extract with an aqueous solution of selected characteristics and a subsequent separation of the two phases. If effective, the analyte of interest should remain at a similar concentration to that in the pre-scrubbed organic solution but the interfering species should be reduced in concentration to a level at which they no longer cause analytical problems in the organic phase. This situation can be encountered when techniques such as spectrophotometric analysis are employed. While enrichment of one

element in the presence of an excess of an interfering element may be possible there may still be absorption at the analytical wavelength due to the undesired species if its concentration is not reduced sufficiently (Appendix A3).

In some situations the concentration of the extracted analyte is not determined in the organic phase. There may be a preference for analysis in an aqueous solution or there could be problems with the organic extract, such as instability, loss on storage or sampling difficulties. Back extraction, the removal of the analyte from the organic extract to an aqueous phase, may be required. The conditions for a favourable back extraction are the opposite of those for the initial extraction. Two approaches, exhibited in this research project, are common. The extractant may be destroyed or the form of the analyte changed.

It should be pointed out, apart from any considerations about the instrumental method employed in the final determination, that the utilization of solvent extraction procedures in any analysis must be examined under practical working conditions. The value of the distribution ratio D for a system can be markedly changed with but minor changes in the aqueous solution being examined. Although there may be an attempt to standardize extraction conditions any slight difference in the original aqueous samples can lead to difference in results. For this reason, unless a calibration curve is validated for the specific circumstances of extraction as well as the detection technique, it is advisable to use a method of standard additions[125] in any trace analysis scheme.

Ion Pair Extractions

The degree to which a basic extractant such as DPPM is protonated and able to form an ion-pair with an anion, and the extent to which this ion-pair may be extracted into the organic phase so as to be separated from the aqueous phase, are influenced by a number of factors. A large number of equilibria are involved within and between each phase, and, in general, the treatment is complicated further by the high concentration of electrolytes present. However, if activity problems may be disregarded, the essential steps can be formulated.

Let it be assumed that the basic extractant, B, is introduced in the organic phase and equilibrated with an aqueous phase containing protons (hydronium ions), H^+, and anions, A^-. This could be an aqueous acidic solution such as HCl. Two models of the extraction process, equivalent from a thermodynamic viewpoint, may be used to explain the extraction.[126] One model assumes that equivalent amounts of protons and anions are first transferred from the aqueous to the organic phase where they then associate with the extractant to form the ion-pair complex. This model seems the least suitable when describing amine extractions although some researchers regard it as mechanistically the more logical approach. In the second approach it is assumed that B must initially become distributed in each phase

$$\overline{B} \rightleftharpoons B \qquad K = [B]/[\overline{B}] \qquad (2.25)$$

Protonation occurs in the aqueous phase

$$B + H^+ \rightleftharpoons BH^+ \qquad K = [BH^+]/[B][H^+] \qquad (2.26)$$

Next, ion-pair formation becomes possible

$$BH^+ + A^- \rightleftharpoons BH^+A^- \qquad K = [BH^+A^-]/[BH^+][A^-] \qquad (2.27)$$

The ion-pairs are distributed between the two phases

$$BH^+A^- \rightleftharpoons \overline{BH^+A^-} \qquad K_d = [\overline{BH^+A^-}]/[BH^+A^-] \qquad (2.28)$$

If this accurately represents the situation the extraction equilibrium of the system is equivalent to:

$$\overline{B} + H^+ + A^- \rightleftharpoons \overline{BH^+A^-} \qquad (2.29a)$$

and

$$D = K_d = [\overline{BH^+A^-}]/[\overline{B}][H^+][A^-] \qquad (2.29b)$$

provided one assumes that any further dissociation or polymerization in the organic phase is negligible.

A plot of $\log[\overline{BH^+A^-}]$ vs. $\log[\overline{B}] \times a_{HA}$ should be a straight line of slope +1, where a_{HA} represents the activity of the acid. If, on the other hand, the ion-pair in the organic phase were to dissociate, the log-log plot could have a slope as low as +½. If polymerization prevails, the degree of polymerization would be reflected in the slope and the value of this slope would be greater than +1.[112]

It follows that there are two essential factors which determine the extent of any anion extraction. One is the nature of the ion-pair formed in the aqueous layer. The other is the partition of either the uncharged complex or of the ion-pair.

The ion-pair formation may be treated as an equilibrium reaction with the free-energy of ion-pairing expressed as:

$$\Delta G_{ip} = -R\ T\ \ln K_{ass} \qquad (2.30)$$

where, according to Bjerrum's theory the associaton equilibrium constant

$$K_{ass} = \frac{4\pi N}{1000} \left(\frac{Z^2e^2}{\epsilon kT}\right)^2 Q(b) \qquad (2.31)$$

Cr(III) does not extract into DPPM/$CHCl_3$ from HCl solutions,[74] the extraction using other diluents was checked. However, of more concern is the possibility of the extraction of anionic Cr(III) complexes. Certainly anionic Cr(III) oxalato complexes have been extracted by tertiary amines.[150,168] Therefore, ^{51}Cr(III)-oxalato complexes were used as a model in an examination of such extractabilities into DPPM/diluent. A Cr(VI) complex not normally found in the various acidic solutions was also of interest - the peroxychromic acid complex. The generation and extraction of this complex in HCl solutions was investigated.

A clean separation of the organic and aqueous phases for the different diluents and aqueous acidic solutions was considered important. Both manually and mechanically mixed systems were separated by gravity or by using a centrifuge and examined for problems or differences due to the procedures employed.

For all of the extraction systems the nature and stability of the extracted chromium complex was investigated. This was done by separating the organic phase containing the ^{51}Cr from the aqueous phase and placing it in a sealed vial made of clear glass, amber glass or these glasses after silanization. The organic phase was stored by itself or in contact with water, a pure acid solution of desired concentration, a sodium or potassium hydroxide solution, or various reducing agents. Storage was under ambient conditions or at a controlled temperature. Aliquots of the organic phase, and the aqueous phase if present, were counted at different times. The container itself was counted after removal of part or all of the contents to determine if

there was any loss of activity to the container walls. Aliquots of the solutions were also examined on ion-exchange resins, alumina or silica gel at different times to determine whether or not changes were occurring during storage.

High specific activity ^{51}Cr was added to environmental samples so that the extraction of such solutions could be examined by tracer techniques as well as by AAS. The labelled samples were left at room temperature for various times and monitored to determine whether or not secular equilibrium had been achieved. Of specific concern were any differences in behavior of the real samples and the ideal solutions utilized in the laboratory in the development and assessment of the extraction procedure with DPPM.

3.3 The Analysis of Equilibrated Samples

3.3.1 Determination of the distribution of diphenyl-2-pyridymethane complexes

The protonation of DPPM is essential to the extraction process. To be able to understand the system the concentration of acid in both the aqueous and organic phases must be determined. Further, if it is possible with a working system, it would be advantageous to be able to find the actual concentration of each type of protonated DPPM, whether it be in the aqueous phase or organic phase.

For acid-base titrations, solutions of potassium hydroxide were prepared by either diluting a concentrated solution of KOH or dissolving KOH pellets directly in boiled deionized water. The solutions were stored directly in polyethylene bottles or stored after having passed

through an anion exchange column in the hydroxide form. The solutions of appropriate concentration were standardized against a primary potassium hydrogen phthalate solution to a phenolphthalein indicator end-point. The KOH solutions were transferred quickly to a microburet for use in titrating acidic solutions. Since the standard KOH solutions were prepared approximately each week and stored in sealed containers there should be negligible uptake of atmospheric carbon dioxide.[169] There was no indication of any determinate error due to a carbonate formation problem.

While the standard KOH solutions were used in the determination of acid concentrations in common aqueous solutions they were most extensively employed in the examination of various fractions in the solvent extraction experiments. The aqueous acid concentration was commonly checked both before and after equilibration of the organic and aqueous phases. The acid content of the organic phase was determined by a two phase titration. The end-point as determined by the color change of the phenolphthalein indicator was found to be as reliable as that determined by employing a pH meter and, being much simpler, was adopted in all analyses. Although immiscible "globules" did form in the two phase titrations, the mixing procedure and careful observation assured that a true end-point was achieved. Therefore, a procedure involving addition of a mutual solvent, acetone, in the two phase titrations, while investigated, was of little advantage, increased handling, introduced another source of error and was rejected.

In the examination of the extraction of an inorganic acid the initial acid concentration of the aqueous phase must represent the

concentration of that acid in its molecular form, [HX], and/or its dissociated form as protons, $[H^+]$. After the solvent extraction process the aqueous phase may contain several acidic species; [HX], $[H^+]$, $[DPPMH^+]$ and [DPPMHX]. The titration reveals only the total concentration of all of these species. However, the difference between the initial acid concentration and the concentration after an extraction experiment should reveal how much acid has been extracted into the organic phase. The concentration as determined by this difference should coincide with that as determined by the two phase titration of the separated organic phase. This total acid concentration in the organic phase, which must represent $\overline{[H^+]}$, $\overline{[HX]}$, $\overline{[DPPMH^+]}$ and $\overline{[DPPMHX]}$, was evaluated by both methods. However, the direct determination in the separated organic phase was chosen for routine analyses. This evaluation of sometimes very low acid concentrations directly is subject to less error than would be expected in taking the difference of comparatively very large acid concentrations as determined in a different phase.

The solubility of an acid in an organic diluent was determined by equilibrating the aqueous acid with the pure solvent, separating the two phases, and performing a two phase acid-base titration on an aliquot of the organic phase. The values so obtained, $\overline{[H^+]}$ plus $\overline{[HX]}$, would not be expected to change in the presence of DPPM. Therefore, it should be possible to approximate the amount of DPPM protonated in the organic phase in an extraction process. The direct acid solubility concentration in a diluent may be subtracted from the total acid concentration in the organic phase after equilibration of the same

aqueous acid solution with DPPM/diluent to evaluate $\overline{[DPPMH^+]}$ plus $\overline{[DPPMHX]}$.

It is not as easy to determine the concentration of DPPM protonated in the aqueous phase. However, a method was developed to evaluate these concentrations in actual extraction experiments. This was based on the observation that in the presence of $HClO_4$ in a specific concentration range there was virtually total extraction of the DPPM complexes into the organic phase. Certainly with 1M $HClO_4$ all of the DPPM ended up in the organic phase in a protonated form. This method developed to determine the concentration of DPPM complexes in the aqueous phase involves the following steps:

1. Equilibrate then separate the two phases involving aqueous HX and DPPM/diluent.
2. Add concentrated $HClO_4$ to an aliquot of the aqueous phase to make the solution 1M in $HClO_4$. Note: when there is a sufficient concentration of complexed DPPM in the aqueous phase this addition of $HClO_4$ causes a rapid visible change. The clear solution becomes opaque, even milky, when the concentration is very high.
3. Add an aliquot of pure diluent and equilibrate the new system. Note: the aqueous layer immediately becomes clear.
4. Separate the two phases and titrate a portion of the organic phase with a standardized solution of KOH to a phenolphthalein indicator end-point.
5. Calculate the concentration of DPPM complexed in the aqueous phase of the original extraction system, assuming stoichiometric formation and extraction of $DPPMHClO_4$ and neutralization by KOH, and knowing the

measured volumes of solutions employed at each stage.

3.3.2 Spectral analysis.

UV/visible spectra

Solution absorption spectra were obtained using matched 10 mm quartz or high quality optical glass absorption cells, with the reference cell containing the pure solvent or solution prepared identically to the sample solution except that the analyte in question was absent. For all solutions a complete scan over the spectral region was first recorded so as to identify the wavelengths of interest. Thereafter, samples to be studied were examined by either complete scans or scans of particular regions, to check for changes in spectra. To follow the kinetics of a reaction or determine the absorbance of solutions at different concentrations the system was monitored at a fixed wavelength. The spectra of DPPM were examined in aqueous solutions and in the different organic diluents of interest. It was hoped that this would assist in ascertaining the distribution of DPPM after the solvent extraction had been completed. Unfortunately, this was of little value for the working systems using 0.100M DPPM/diluent. The most appropriate concentration range for spectral analysis was established by diluting the standard 0.100M DPPM/diluent. For the absorption maximum at λ = 263 nm this proved to be at a concentration near 1×10^{-4} M.

The determination of the ionization constant for $DPPMH^+$ was done according to the procedure described by Albert and Serjeant.[170] Since DPPM is very insoluble in water a stock solution of 3.016×10^{-4} M DPPM was prepared in 3.04×10^{-2} M HCl. This solution was used in the

preparation of 1.005×10^{-4} M DPPM solutions. The extinction coefficient of DPPM was established by examining the absorbance in 0.02 to 1.0 M KOH. For $DPPMH^+$ the absorbance was found in 0.01 to 0.4 M HCl. Buffer solutions of pH 4 to 5, composed of sodium acetate/hydrochloric acid of total ionic strength 0.030 M, were used to determine pK_{DPPMH^+} by spectrophotometry.

Using samples with an absorbance in a reasonable range for the instrument a number of extraction systems containing only an acid in the aqueous phase were examined. The absorbance of the DPPM complexes in both the aqueous and organic phases were monitored.

The DPPM/diluent extractions of Cr(VI) from aqueous acidic solutions were investigated in some detail. There were two primary objectives - to examine the spectra and any fine structure therein and to see if the extractions could be of value in the analysis of chromium in the mg/L (ppm) concentration range. Samples containing Cr(VI) of the desired concentrations in the acidic solution, most often HCl, were sometimes labelled with ^{51}Cr so as to follow the extraction radiometrically as well as spectrophotometrically. A number of extraction ratios were employed. The spectra were examined over the total accessible wavelengths with particular attention being focused on any regions exhibiting any fine structure. Calibration curves were prepared for Cr(VI) in the low ppm concentration range. The spectral stability of the extracted Cr(VI) complexes were monitored.

Several other chromium complexes were investigated spectrophotometrically. The Cr(III) oxalato complexes, particularly the anionic ones, were examined in the presence of acids to determine their

stability and their extractability by DPPM. The effect of hydrogen peroxide on an acidic chromate solution was checked. The formation of the peroxychromic acid and its extraction by DPPM/diluent was too rapid to be followed by the experimental techniques employed but the reduction of the species in the extract was monitored.

The spectra were taken of several elements which were considered as potential interferences in the analysis of Cr(VI) by a DPPM/diluent extraction (Appendix C).

Infrared spectra

Infrared spectra were obtained for samples of the diluents $CHCl_3$, CH_2Cl_2 and CH_2ClCH_2Cl between the two KBr windows of a sealed sample cell of measured path length 1.04 mm. With the diluent used as the background reference the spectra were obtained for 0.10M DPPM/diluent and 0.10M DPPM/diluent after equilibration with a number of aqueous solutions. Most attention was paid to the extracts from 1.0M HCl and 1.0M HCl containing fixed amounts of Cr(VI), added as $(NH_4)_2CrO_4$, $K_2Cr_2O_7$ and $KCrO_3Cl$. Spectra of the organic extract from pure water, 1.0N H_2SO_4 and 1.0N H_2SO_4 containing Cr(VI), 1.0M $HClO_4$, 1.0M HNO_3 and 1.0N H_3PO_4 were also obtained.

When using the Unicam SP 1100 Infrared Spectrophotometer the sample and background cells were matched as well as was possible. With the Nicolet 7199 FT-IR instrument the identical cell was used throughout with careful preparation between sample analysis. However, the samples from the extraction of Cr(VI) in H_2SO_4 proved particularly troublesome. These required the dismantling of the cell and repolishing. Therefore, in any series of experiments the extractions from H_2SO_4 were run last.

Some variations on these procedures were undertaken in an attempt to allow those absorptions due to Cr(VI) species in the organic extract to stand out against the major absorptions of the DPPM/diluent system. The concentration of the DPPM was changed and alternative samples were used as the background.

Once familiar with the operation of the FT-IR system it was adopted for detailed analysis. Of the several advantages of infrared interferometry, as reported at a recent Nato Advanced Study Institute[171], the convenience of computer manipulation of spectra and the accurate assignment of band positions were most important in the examination of the DPPM extracts. One hundred scans were employed to minimize random interferences in spectra. Spectra were stored and compared so as to focus on particular regions of interest.

3.3.3 Analysis by atomic absorption spectrometry

In the analysis of both organic extracts and aqueous solutions containing chromium the sample introduction was by direct injection of from 5 µL to 20 µL of solution. With the volatile extracts this required extreme care to provide a replicate sample. The pipet system was first saturated with the vapor of the diluent then a check run for reproducibility of the instrumental response with injection of a given sample.

Since with the initial DPPM/$CHCl_3$ extractions the enrichment factor for different natural waters varied somewhat a systematic approach using a standard addition method (continuous variation of standard at constant total volume[125]) was required for each ETA-AAS

chromium analysis. However, for the more efficient extraction using 0.10M DPPM/CH_2ClCH_2Cl a calibration curve was prepared by extracting Cr(VI) from standards made in deionized water and HCl and measuring the chromium signal in the organic samples. In this instance it was possible to estimate the chromium content in a natural water from the absorption signal obtained from its extract in an identical manner.

The analytical method permitted an evaluation of the Cr(VI) content in an aqueous sample both before and after a Ce(IV) oxidation procedure. Thus, Cr(VI) in solution, if any, could be determined then the total chromium content could be estimated. Of course the Ce(IV) oxidized the chromium present in the reagent grade hydrochloric acid used, but since this research program focussed on method development rather than on environmental analysis it was considered adequate to compensate for this chromium by subtraction.

3.4 Data Management

The conversion of data into chemically useful information and the evaluation of its reliability can be a formidable task. The general statistical analysis that was adopted is representative of that outlined by Skoog and West.[169] Most calculations were completed on a TI Programmable 58C calculator (Texas Instruments), using the standard programs for the determination of means, standard deviations, correlation coefficients, etc. Some data reduction and curve fitting were done on an Apple IIe computer (Apple Computer). Extra digits were often carried through the calculations to avoid cumulative round-off errors but significant figures are reported in the final results.

Although it would be desirable to evaluate the uncertainty of each parameter that is involved in any experiment it is not practical unless one is prepared to sacrifice large amounts of data in favor of many fewer but oft repeated experiments. Therefore, uncertainties which were due to volume and weight measurements, mixing times, temperature fluctuations, instrumental responses, etc. were not dealt with separately but were considered to be an inherent incertitude in the overall result.

In practice, most results are based on radiometric counting and uncertainties were calculated from counting statistics alone.[172] While multiple separate counts were used to determine the mean and uncertainty for the activity of a single sample in a few cases, this proved to be very time consuming and of little advantage when compared to the standard practice of counting the sample once for the desired period of time and approximating the uncertainty by taking the square root of the total number of counts.[178] The activity displayed instrumentally, A_i, was corrected for the background, B, by simple subtraction. Therefore, the corrected activity of a sample, A_i', is

$$A_i' = A_i - B \qquad (3.2)$$

For example, with a 1 mL sample of an organic extract the results, including the standard error, are:

$$\overline{A_i} = 11487 \pm \sqrt{11487} = 11487 \pm 107 \text{ c/min}$$

$$B = 129 \pm \sqrt{129} = 129 \pm 11 \text{ c/min}$$

$$\overline{A_i}' = (11487 \pm 107) - (129 \pm 11) = 11358 \pm 108 \text{ c/min}$$

the uncertainty in the result is determined according to standard error propagation rules as the square root of the sum of the squares of the

uncertainties in the individual values (ie. $\sqrt{[(107)^2 + (11)^2]}$ = $\sqrt{[11487 \pm 129]}$ = 108).

Assignment of the relative concentrations of chromium in analyte fractions by comparing the activity in equal volumes of solution counted under identical circumstances usually introduces little uncertainty. However, when examining the extraction of $^{51}Cr(VI)$ by an equal volume of 0.1M DPPM/diluent, if the distribution ratio, D, is large, there is a problem in that the activity in a 1 mL sample of the aqueous phase, A_i, has a large uncertainty; ie. the count is only marginally greater than the background, B.

eg. If D = 581 and $\overline{A_i}' = 11358 \pm 108$ c/min

$A_i' = \overline{A_i}'/D = 11358/581 = 20$ c/min

It follows that

$A_i = A_i' + B = 20 + 129 = 149$ c/min

and the corrected activity should be reported as

$A_i' = 20 \pm 17$ c/min.

To overcome this limitation without resorting to the use of samples with extremely high radioactivity, extractions were performed using 5.0 mL of the labelled aqueous phase and 2.0 mL of the organic phase. By counting 4.0 mL of the separated aqueous phase for 5 minutes sufficient counts were obtained to reduce the uncertainty in the calculated value of A_i'. However, by counting unequal volumes of the aqueous and organic phases a correction for the detector response had to be introduced. For 4.0 mL of solution this was 1.043; ie. 4.0 mL containing a given activity would exhibit 1.043 times as many counts if reduced in volume to 1.0 mL.

Continuing with the example, 4.0 mL of the aqueous phase had an activity:

$$A_i'(4\ mL) = (1020 \pm 32) - (645 \pm 25) = 375 \pm 41\ c/5\ min$$

However, to calculate D all activities must be reported on a common basis (counts min^{-1} mL^{-1}) since

$$D = [\overline{Cr}]/[Cr] = \frac{^{51}\overline{Cr}/\overline{V}}{^{51}Cr/V} \qquad (3.3)$$

$$D = \frac{(11358 \pm 108\ c/min)}{(1\ mL)} \Big/ \frac{(1.043)(375 \pm 41\ c/5min)}{(4\ mL)}$$

$$= 581 \pm 64$$

Again the uncertainty is determined according to standard error propagation rules (ie. $\sqrt{[(108/11358)^2 + (41/375)^2]} = 0.110 \times 581 = 64$).

However, when graphically representing the distribution ratio as a function of the aqueous acid concentration it is most convenient to use log D values. The uncertainty in log D is most properly given by evaluating log D for each of the extremes defined by the range of D ± uncertainty. Since the logarithmic function is non-linear, this generates assymetric bounds for the range of log D; e.g. log 581 = 2.764, but considering the uncertainty of ± 64 the range of log D is 2.713 to 2.810.

Another circumstance that required a correction when assigning the proportions of chromium present in a sample by radiometric counting alone was when an analysis continued for an extended period of time. For instance, when changes in a system were being examined over time by removing an aliquot of solution either all of the samples had to be saved to be counted at the same time or a correction applied for the decay of the ^{51}Cr. The activity, A, at any time can be calculated from

the equation:

$$A = A_o e^{-\lambda t} \qquad (3.4)$$

Since the half-life of ^{51}Cr is relatively long, $t_{\frac{1}{2}} = 27.8$ d, this correction became important only when an experiment extended beyond several hours.

Data generated by other analytical procedures, such as titration methods or spectrophotometric and AAS analysis, were treated in a conventional manner. In experiments where there were replicate trials the mean and standard deviation could be calculated. However, many experiments were unique. The consistence of the results could be assessed by comparison to the related experiments but the uncertainty in any one data point could be estimated only by examining the precision of the method. While recognized, there is no attempt to represent such uncertainties in all instances.

The important results of many experiments are displayed in a graphic form. Error bars representing the uncertainty have been included only when the uncertainty is larger than the size of the symbol used in marking the position of the point.

When a graphical representation is for an apparently linear relationship it shall conform to the equation

$$y = mx + b \qquad (3.5)$$

where y represents the dependent and x the independent variable, m is the slope and b is the intercept. For such graphs the slope and intercept of the best straight line passing through the points have been calculated by the least squares method of linear regression. The correlation coefficient, r, has been determined using the standard

program as well. Perfect correlation between the experimental data and the line yields r = ±1.000. In a like manner, the fitting of data to a theoretical equation of higher order is often possible. Again, the correlation coefficient may be determined and both the original data and the theoretical curve can be represented in a graphical fashion.

We abstract from the phenomenon that which is peculiar to the position and motion of the observer; but can we abstract that which is peculiar to the limited imagination of the human brain.

A. S. Eddington

4. RESULTS AND DISCUSSION

4.1 Preparation of ^{51}Cr and its use in examining reactions of chromium

4.1.1 Preparation of ^{51}Cr

The irradiation of $(NH_4)_2CrO_4$ with thermal neutrons was undertaken to explore the possibility of producing high specific activity ^{51}Cr of a reasonable yield in a short time. One immediately apparent advantage of using $(NH_4)_2CrO_4$ instead of the alkali metal chromates commonly used in this process[173,174,175,176] was that superfluous radioactivity was much lower. Because of the induced activity of the alkali metal cations, cooling times have to be prolonged or the handling of substance with considerable activity not due to the desired ^{51}Cr has to be accepted. Further, with the alkali metal chromates the yield of the separated enriched ^{51}Cr fraction does not exceed 11%[173] so that the bulk of the activity created is in the unenriched fraction and is simply disposed of. Therefore, to achieve the desired product most researchers opt for irradiations of about a week and a cooling period at least as long.[174,175] However, it is known that the enrichment factor of the enriched species decreases with an increase in the irradiation time[177] and with the length of storage where products are subject to annealing processes.[163,178] The short irradiations and prompt separations and assays which are possible with $(NH_4)_2CrO_4$ could overcome such limitations.

While preparation of ^{51}Cr employing the hot atom process was

undertaken when the tracer was needed, a careful analysis of the product was performed in only a few cases. However, the proportion of the radioactivity in the cationic and anionic fractions was generally checked. On the basis of eight trials, it was concluded that 81.2 ± 0.8% of the radioactivity resides in the Cr(III) fraction when reagent grade $(NH_4)_2CrO_4$ is irradiated directly or after recrystallization.

The initial separations of the Cr(III) and Cr(VI) were accomplished by ion-exchange procedures. As long as the irradiated $(NH_4)_2CrO_4$ was dissolved in an acidic solution, from 0.02M to 1.0M HCl was used as well as 0.1M HNO_3 in one trial, the separations were effective. The concern about the possibility of reduction of the Cr(VI) in an acidic solution, which would lower the specific activity of the Cr(III), prompted an attempt at the separation of the irradiated chromate when dissolved in water alone. The target chromate was dissolved in water and small portions were placed on the AG1-X8(Cl^-) resin at different times after dissolution, to be eluted with water.

time(h)	0.50	0.83	5.42	29.92	124.58
$\frac{^{51}Cr\ eluted}{^{51}Cr\ total}$	0.258	0.221	0.144	0.042	0.018

The eluted fraction never achieved the proportion of the activity experienced with dissolution in acidic solutions. The Cr(III) produced in the recoil process must have been gradually lost to container walls and/or converted to chromium of the type CrO_2^-. Since the solution was slightly basic, pH 7.5, this could be predicted from adsorption studies

and Figure 2.1a. Upon acidification the cationic fraction approached the 80% expected.

The separation of the enriched $^{51}Cr(III)$ from the target chromate using 0.10M DPPM/$CHCl_3$, as reported by Iqbal and Ejaz[174], was reasonably successful with the four recommended extractions. However, by dissolving the irradiated $(NH_4)_2CrO_4$ in 0.6M HCl and employing 0.1M DPPM/CH_2ClCH_2Cl as effective a separation was achieved in two stages. Three separate trials for this improved extraction were completed. The extraction ratio, $V/\bar{V}$, was varied from 0.4 to 1, but since the extraction was so efficient this made little difference in the amount of activity removed from the dissolved target solution. Using as an example one trial in which the initial activity of 2.0 mL of the aqueous target solution was 478400 ± 3000 c/min, the first extraction removed 86800 ± 650 c/min. Visually, the aqueous phase went from the normal chromate color to an almost colorless solution with the one extraction. Of course the organic phase became yellow. The second extraction resulted in an activity in the organic phase of 194 ± 17 c/min. It was concluded that essentially all of the chromate had been removed by the first extraction and primarily Cr(III) remained in the aqueous phase. A third extraction provided an activity of 136 ± 22 c/min in the organic phase. Since the aqueous phase contained chromium providing an activity of 391400 ± 2800 c/min this last extraction reflected mainly the presence of Cr(III) rather than residual Cr(VI) still being removed. Thus, in this trial the enriched Cr(III) fraction contained 81.8 ± 0.8% of the activity. For the other two trials results were similar, 80.4 ± 1.6% and 80.7 ± 1.0% of the activity was in the aqueous phase after the

extractions. In all cases these proportions were in good agreement with the assignment by ion-exchange procedures.

The enrichment factor, which may be defined as the ratio of the specific activity of the enriched fraction to that of the unseparated target, was determined by two methods. In one case, with a sample separated by ion-exchange procedures, the concentration of the Cr(III) fraction was estimated by spectrophotometric means after oxidation to the chromate. While the original $(NH_4)_2CrO_4$ target was made up in solution to 0.04M the Cr(III) fraction had a concentration of about 2.8 x 10^{-5}M (1.5 ppm). By comparing the activities in equal volumes of solution:

$$\text{Enrichment Factor} = \frac{(22870 \text{ c/min})}{(2.8\times10^{-5}\text{M})} \Big/ \frac{(28300 \text{ c/min})}{(0.040\text{M})} = 1150$$

The second analytical approach utilized the aqueous phase after the extraction by 0.10M DPPM/CH_2ClCH_2Cl. The original $(NH_4)_2CrO_4$ target was made up to 0.030M while the aqueous phase was estimated at 1.5 ppm by AAS.

$$\text{Enrichment Factor} = \frac{(144800 \text{ c/min})}{(2.9\times10^{-5}\text{M})} \Big/ \frac{(174800 \text{ c/min})}{0.030\text{M}} = 860$$

These enrichment factors, while significant, were less than desired and provided for a specific activity of only about 1 mCi/mg; ie. the very high specific activity hoped for was not attained with $(NH_4)_2CrO_4$. Tsai and Teh[176] had been able to achieve an enrichment factor of only 150 for $(NH_4)_2CrO_4$. While the shorter irradiations in this study did improve the enrichment there must still be a problem attributable to decomposition or annealing during the nuclear

bombardment. Certainly in an irradiation lasting days there was an obvious decomposition problem. The influence of annealing, only recently coming under Stamouli's scrutiny[178], is unclear. However, Tominaga and Tachikawa[163] regard it as one of the most important topics in solid state hot atom chemistry. An understanding of such effects could lead to significant improvements in the production of enriched ^{51}Cr by a Szilard-Chalmers process.

The decision was made to pursue this enrichment problem no further, even though it was tempting to see if the short irradiations and prompt separations by the DPPM/CH_2ClCH_2Cl extraction could improve upon the best enrichments so far achieved, about 30 mCi/mg[173,174,175], with the irradiations of the alkali metal salts. The advantage of the efficient and clean removal of the bulk of the ^{51}Cr activity in the lower organic layer by the extraction technique is obvious. Long cooling periods would not be needed since the separation is so easy; it could be done by remote control if necessary. The irradiation of $(NH_4)_2Cr_2O_7$ should also be considered, it would have all the advantages of the $(NH_4)_2CrO_4$ but could be more stable.

4.1.2 Reactions of chromium

When $^{51}Cr(III)$ was needed the enriched product from the Szilard-Chalmers reaction was used or the high specific activity radiochromate was reduced. The procedure adopted for this reduction in trace analysis work used 5.0 mL of 1 x 10^{-3} M HCl and 0.05 mL of 30% H_2O_2. The solution was warmed in a Teflon or pyrex beaker and boiled to destroy excess peroxide. The sample stored in 1 x 10^{-3} M HCl remained

totally cationic. This simple procedure is recommended as the method of choice for the reduction of Cr(VI) in trace analysis work since it is easier to attain a quantitative reduction than by the sodium sulfite reductions sometimes advocated.[56,73]

Ce(IV) was found to be the most effective oxidizing agent for converting trace amounts of Cr(III) to Cr(VI). Fisher certified ceric sulfate solution N/10 was convenient to use and oxidation was completed in HCl solutions without the boiling step recommended by Tanaka and Ishimaru[72] or Yoshimura and Ohashi[49]. The $^{51}Cr(III)$, at a concentration near 1 ppb in 1M HCl solutions, was oxidized completely by 1×10^{-3} M Ce(IV) within ten minutes at room temperature. When solutions were prepared with deionized water the $^{51}Cr(VI)$ was stable for at least a day but when natural waters were used reduction occurred sooner (Appendix B).

The success of the Ce(IV) oxidation and the ease with which it can be accomplished makes it the method of choice for use with environmental samples in which total chromium is to be determined after oxidation to Cr(VI). If the separated chromium is to be analyzed in the final stage by a technique such as AAS which is element specific then the presence of any Ce(IV) should cause little difficulty. However, in spectrophotometric methods it is recognized that Ce(IV) is one of the most serious interferences in a chromate analysis.[179,180] In this instance the Ce(IV) may be destroyed by sodium azide[179] or the oxidation of Cr(III) may be achieved by using H_2O_2 in an alkaline solution.

In many of the solutions examined the reduction of Cr(VI) when at trace levels was a source of potential difficulty in any analysis.

Above pH 6, where the principle species is the CrO_4^{2-} ion, there was no evidence of reduction with labelled samples. However, lowering the pH caused a reduction of this Cr(VI) and the rate of reduction increased as the pH decreased. This reduction rate also increased with an increase in temperature. Further, by lowering the initial concentration of Cr(VI) the proportion of the activity found in the Cr(III) fraction became greater at a given time after sample preparation (Appendix B).

The reduction of Cr(VI) on anion-exchange resins was not appreciably different from that in solution (Appendix B).

Because of the concern that in chromium speciation it could be possible to misinterpret results if anionic Cr(III) was neglected, the separation of the Cr(III) oxalato complexes from solution was compared to that of Cr(VI). By using the DPPM extraction system Cr(VI) was extracted into the organic phase leaving both cationic Cr(III) and the anionic Cr(III) oxalato complexes in the aqueous phase. This lack of extraction of the anionic Cr(III) oxalato complexes was not due to the conversion to cationic species in the time of extraction since the dissociation in 1M HCl is comparatively slow. On the other hand, the ion-exchange procedures employed were not satisfactory in separating anionic Cr(III) from Cr(VI). However, the Ce(IV) oxidation of such complexes was possible so that a total chromium analysis, based on the extraction of Cr(VI), could be completed (Appendix B).

4.1.3 The loss of chromium to container surfaces

In most of the experiments conducted with Cr(VI) this oxidation state proved to be extremely resistant to loss to container surfaces.

However, stainless steel needles picked up considerable activity when handling high specific activity $^{51}CrO_4^{2-}$. Plastic Eppendorf tips picked up a maximum of 0.3% of the activity so were adopted for use throughout the research program. Ordinary glass and plastic containers, except under conditions where some reduction of Cr(VI) occurred, did not register any appreciable activity after contact wit Cr(VI) solutions. A 10 ppb $^{51}CrO_4^{2-}$ label introduced into natural waters was not lost to the container walls or changed from the anionic form. For instance, in ocean water at pH 8 there was no loss of activity from solution in 5 days to containers made of pyrex glass, silanized glass, polypropylene or polyethylene. In 3 weeks loss was still insignificant and even after 3 months it was less than 5% in any container when left at room temperature.

With Cr(III) adsorption losses became more significant. This wall loss depended upon several factors, the master variable being pH. At pH < 3 there was negligible loss of ^{51}Cr activity from solution but as the pH was increased the loss became more significant.

With an ionic strength increase in a solution the loss of $^{51}Cr(III)$ activity to the container walls decreased. The addition of salts may add ions which compete for the surface adsorption sites or lead to some stabilization of the chromium by complexation. Since the rate of loss of Cr(III) to containers depends upon the ionic strength of the solution, and in environmental samples this can vary appreciably, this becomes another concern in speciation experiments.

A number of containers made of different materials were employed in an attempt to minimize the loss of activity to surfaces.

Unfortunately, no container was completely immune to the problem when using 5 ppb $^{51}Cr(III)$ at a measured pH near 5 but an unknown low ionic strength. Polypropylene containers were most satisfactory at room temperature but became subject to substantial loss when heated. This was typical of all synthetic plastics; including Teflon TPF, TPX plastic, polycarbonate and polyethylene. Pyrex glass was used with such samples at elevated temperatures but even then the loss at 70°C was 3.9% in 1 hour and 7.0% in 2 hours. Silanization of the glass was of little benefit.

Similar experiments were conducted with 1×10^{-6} M Cr(III) complexed with the oxalate ion. After heating the solution for 4 hours at 70°C the loss of activity to the walls never exceeded 1%. This was interpreted as a reflection of the stability of these complexes. While Cr(III) could be lost to the container walls, once complexed the chromium remained in solution.

Another factor which influences the extent to which activity is lost to container walls is the total amount of Cr(III) present. Qualitatively the loss of ^{51}Cr from solution was always a greater problem when the total chromium concentration was lower. This was most apparent in an experiment in which equal amounts of the $^{51}Cr(III)$ tracer were placed in four 4 mL glass vials and slowly evaporated to dryness in the presence of ordinary $Cr(NO_3)_3$, from about 1 to 5×10^{-8} moles, and 1.0×10^{-7} moles of $C_2O_4^{2-}$. The container was filled with 1 mL of water, sealed and a mixing/heating (70°C) procedure was undertaken for 3 hours. Each vial was opened and the proportion of the sample in the cationic and anionic forms determined by ion-exchange procedures.

However, it was immediately apparent that the activities of the dissolved portions were less than expected. The bulk of the activity was found to reside on the container walls. The mixing procedure was conducted for an additional 3 hours with but negligible changes in the results. Assignment of the average ^{51}Cr activity to the anion and cation protions in solution and to the container walls may be summarized.

moles Cr^{3+} added	% anionic	% cationic	% vial surface
0 (tracer only)	3.1±0.1	1.0±0.1	95.8±0.1
1.2×10^{-8}	16.9±0.8	2.5±0.4	80.5±0.4
2.3×10^{-8}	48.2±0.1	5.5±1.9	46.2±1.9
4.7×10^{-8}	27.8±1.1	34.6±0.6	37.6±1.8

To account for these data and corroborating observations, without undue elaboration, a competition model seems appropriate. The reactions of Cr(III) with $C_2O_4^{2-}$ may be competing with the adsorption of the Cr(III) by the glass of the container walls. Although representative reviews of such adsorption phenomenon for metal complexes are available[181,182] it is far from being a fully understood process. However, if it is assumed that there are a limited number of active sites on the glass surface, and if once occupied by a Cr(III) species these sites are no longer capable of adsorption, then the lower glass activity with an increase in the amount of Cr(III) would be reasonable; ie. there is a greater % loss of ^{51}Cr activity to the surface at the lowest Cr(III) concentration. This is in keeping with the statement by Kinninburgh and Jackson[183] that the adsorption tends to be more

important at low cation concentrations.

Further, the longer the Cr(III) remains in solution with an excess of $C_2O_4^{2-}$ the more likely it is to form an anionic complex which is not readily lost to the container walls. This is apparent from the data since the anion/cation ratio increases until the quantity of Cr(III) is more than could be complexed in the most anionic form by the $C_2O_4^{2-}$.

Few reports on the adsorption of chromium on container surfaces are available for comparison to this study. Shendrikar and West[184] have studied the adsorption characteristics of Cr(III) and Cr(VI) on selected surfaces but at a comparatively high concentration of 1 ppm. At pH 6.95 there was a loss of Cr(III) to polyethylene (25%), flint glass (19%) and pyrex (17%) but a loss of less than 1% for Cr(VI) with all containers in 15 days. With Cr(III) there was an apparent induction period of 24 hours before losses occurred. No loss was reported in 0.5% HNO_3 or at pH $\leq$ 3.1.

Nakamura et al.[185] explored the loss of Cr(III) at a lower 50 ppb concentration in similar containers. During storage an exponential decrease of Cr(III) in solution was observed over 15 days in both the glass and polyethylene containers, with a greater total loss in the glass containers. In experiments at different pH values, the maximum adsorption appeared at a pH around 7.5. It was suggested that $Cr(OH)_2(H_2O)_4^+$ was the chemical species adsorbed. Again the Cr(III) could be stabilized by HNO_3 at a pH < 3. The presence of 10^{-4} M EDTA or 10^{-3} M PO_4^{3-} prevented wall loss.

Cheucas and Riley[55] also recognized the storage problem when

analyzing sea water. When samples were kept at 20°C in the dark for 10 days there was loss of a ^{51}Cr tracer to glass containers but not to a polyethylene container.

While most points are in general agreement, neither in this project nor in the report by Nakamura et al.[182] is there confirmation of an induction period before there is a loss of Cr(III) as reported at the higher 1 ppm concentration[184]. Further, plastics, at least polyethylene[55,185] and polypropylene, do not adsorb Cr(III) at the lower trace levels as well as does glass when at room temperature. The presence of the potential complexing agents such as EDTA and PO_4^{3-}, as well as $C_2O_4^{2-}$, in the prevention of wall loss requires clarification. While the oxalato complexes of Cr(III), once formed, were found to be very effective in preventing loss of Cr(III) from solution, their formation is not rapid enough, at the concentrations of $C_2O_4^{2-}$ employed, to inhibit loss by simply introducing $C_2O_4^{2-}$ into solutions containing Cr(III).

When it comes to the adsorption of cations, such as Cr(III), on not only container surfaces but also naturally occurring sorbates, without doubt, as Kinninburgh and Jackson[183] state "there is a need for more information at environmentally realistic concentrations". Any collection and separation/speciation procedures must consider this problem. The more rapidly a sample is secured for analysis the better.

4.2 The DPPM/diluent Extraction System

4.2.1 The extraction of acids

While the aim of the extraction was to separate and concentrate Cr(VI) from an aqueous solution, and experiments were begun with this endeavor in mind, it became apparent that an understanding of the initial protonation of DPPM and the acid extraction process was essential to explain the Cr(VI) extraction. A fairly general examination of acid extractions was undertaken but the focus was definitely on the conditions under which the Cr(VI) extraction was optimized. Therefore, attention was centered on the extraction of HCl in hopes that a model could be developed for the DPPM/diluent extraction system.

However, before examining the extraction of acids under working conditions a brief description of the general protonation phenomenon with DPPM is in order. The dissociation reaction of protonated DPPM in aqueous solution may be represented by the equation:

$$DPPMH^+ \rightleftharpoons DPPM + H^+ \qquad (4.1)$$

and the ionization constant would be:

$$K_{DPPMH^+} = \frac{[H^+][DPPM]}{[DPPMH^+]} \qquad (4.2)$$

or written in the logarithmic form:

$$pK_{DPPMH^+} = pH + \log\frac{[DPPMH^+]}{[DPPM]} \qquad (4.3)$$

At a concentration of 1×10^{-4} M it is possible, from a study of the spectra of DPPM at various pH values, to determine the value for pK by the methods described by Albert and Serjeant[170], even though there is a slight shift in the absorption maximum with pH changes. Using the transformed equation

$$pK = pH + \log \frac{d - dM}{dI - d} \qquad (4.4)$$

where the optical density (absorbance) of the ionic form is represented by dI and that of the molecular form by dM, the value for pK_{DPPMH^+} is 4.44 ± 0.06 according to the data in Table 4.1. This is in close agreement with the value of 4.41 reported in the literature.[121]

While this kind of spectrophotometric analysis can be very useful it cannot be employed directly in an examination of the acid extraction under the conditions of interest. Rather, the titration of the acidic solutions by a standardized base proved most effective.

Although the extraction of Cr(VI) from $HClO_4$ solutions is not effective the extraction of the $HClO_4$ itself by the DPPM/diluent is of particular interest. It is the most readily extracted of all of the inorganic acids examined. Further, the extraction of $HClO_4$ takes on added importance because this extraction is the basis for the determination of the concentration of DPPM in the aqueous phase after mixing DPPM/diluent with any inorganic acid.

The solubility of $HClO_4$ in the diluents employed is negligible but once DPPM is present the $HClO_4$ is substantially extracted. When an equal volume of the aqueous $HClO_4$ solution was mixed with 0.0998M DPPM/CH_2ClCH_2Cl, separated and titrated with a standardized NaOH

Table 4.1 Determination of ionization constant (pK) of Diphenyl-2-pyridylmethane.

Concentration of DPPM = 1.0×10^{-4} M
Ionic Strength = I = 0.030 M
Analytical Wavelength = 263 nm
Optical density molecular species in 0.02-1 M KOH = dM = 0.479 cm^{-1}
Optical density protonated ion in 0.4 M HCl = dI = 0.755 cm^{-1}

(1) pH	(2) d, cm^{-1}	(3) d-dM, cm^{-1}	(4) dI-d, cm^{-1}	(5) $\frac{dI-d}{d-dM}$	(6) log(5)	(7) pK = pH+(6)
3.89	0.697	0.218	0.058	3.759	+0.575	4.46
4.06	0.675	0.196	0.080	2.450	+0.389	4.45
4.38	0.637	0.158	0.118	1.339	+0.127	4.51
4.62	0.603	0.124	0.152	0.816	-0.088	4.53
4.68	0.594	0.115	0.161	0.714	-0.146	4.53
4.76	0.583	0.104	0.172	0.605	-0.218	4.54
4.80	0.578	0.099	0.177	0.559	-0.252	4.55
						4.51

$$pK^T = pK^M - \frac{0.505\sqrt{I}}{1+1.6\sqrt{I}} = 4.51 - \frac{0.0875}{1+0.277} = 4.44 \pm 0.06$$

solution the following results were obtained:

$[HClO_4]$, M (original)	0.062	0.120	0.369	0.990	1.324	3.9%
$[H^+]$, M (equilibrium)	0.032	0.066	0.278	–	1.221	–
$\overline{[H^+]}$, M (by difference)	0.030	0.054	0.091	–	0.103	–
$\overline{[H^+]}$, M (direct titration)	0.0293	0.0550	0.0905	0.0995	0.0990	0.0998

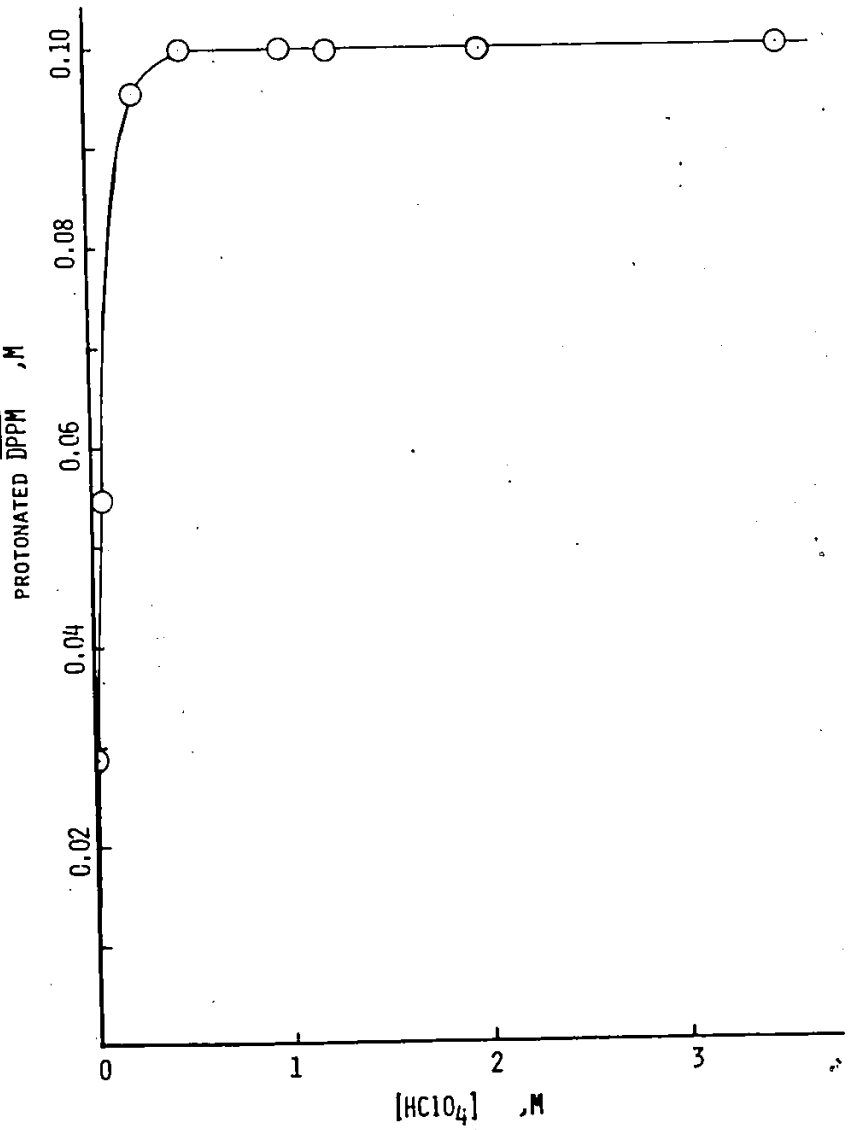
The results from both the direct two phase titrations of the organic phase and the evaluation by finding the loss of acidity from the aqueous phase are in general agreement. However, the direct titration provides for greater precision and seems more reliable, particularly at high aqueous acid concentrations. These data are included also in Figure 4.1. Inspection of this figure indicates that above a $HClO_4$ concentration of about 0.5M the protonation of the DPPM in the organic extract is complete. Certainly up to about 4M $HClO_4$ there is no excess acid removed in the organic phase, only that required by the stoichiometry of the reaction

$$\overline{DPPM} + HClO_4 \rightleftharpoons \overline{DPPMHClO_4} \qquad (4.5)$$

This result is in full agreement with the proposition made by Kedder and Wilson[146] that $HClO_4$ would not be expected to extract in excess, particularly in chloroform like diluents. However, it places in doubt that graphical representation of the extraction by 0.1M DPPM/$CHCl_3$, reported by Ejaz et al.[121], where it appears that there is an excess of acid extracted even below 1M in $HClO_4$.

Figure 4.1

Extraction of $HClO_4$ into the organic phase when mixed with an equal volume of 0.10 M DPPM/CH_2ClCH_2Cl as a function of the initial aqueous $HClO_4$ concentration.


PROTONATED $\overline{DPPM}$,M
0.10
0.08
0.06
0.04
0.02
0
1
2
3
[$HClO_4$] ,M

The behaviour in chloroform and dichloromethane was similar to that in the CH_2ClCH_2Cl diluent. Although, as will be pointed out with the HCl extractions, these diluents do not promote the DPPM protonation in an identical manner, there is still quantitative protonation in the organic phase when the aqueous phase is 1M $HClO_4$.

The fact that $\overline{DPPMHClO_4}$ is produced quantitatively in the presence of 1M $HClO_4$ makes it possible to evaluate the amount of DPPM present in any system by performing a two phase acid-base titration on the organic extract. This was successfully employed to determined the amount of DPPM present in an aqueous phase — addition of pure diluent in the presence of 1M $HClO_4$ leads to extraction of the DPPM which can be analyzed. Results are reproducible and more reliable than the evaluation of [DPPM] from an aqueous phase by a radiolabelling technique.[140]

Even though a detailed examination of acid extractions with other than HCl was not undertaken, the order of acid extractions was established. While $HClO_4$ is extracted most readily, HNO_3 is not far behind. For instance, using 0.90M HNO_3 the organic phase protonation in various 0.10M DPPM solutions was virtually complete: 100% in $CHCl_3$ and CH_2Cl_2 and 97% in CH_2ClCH_2Cl. Even with 0.38M HNO_3 there is 83% organic phase protonation with CH_2ClCH_2Cl and less than 4% of the DPPM remains in the aqueous phase. The HNO_3, like $HClO_4$, not only protonates the DPPM well but also facilitates the ion-pair extraction into the organic phase.

HBr is extracted somewhat less than HNO_3 but better than HCl. Again, as a simple example, with 1.4M HBr about 80% of the DPPM is

protonated in the organic phase when such a solution is equilibrated with 0.10M DPPM/CH_2ClCH_2Cl.

With sulfuric acid there is little protonation in the organic phase. In 1N H_2SO_4 the two phase titration indicates that less than 2% of the DPPM is protonated in the organic phase; ie. $< 2 \times 10^{-3}$ M $\overline{DPPMH^+}$ when 0.10M DPPM/CH_2ClCH_2Cl is used. At the same time the concentration of DPPM in the aqueous phase is an order of magnitude greater. However, Cr(VI) can be extracted from H_2SO_4 solutions and, if at a high enough concentration, significantly effects the proportions of protonated DPPM in each phase (see Section 4.2.2).

Only one organic acid was investigated, acetic acid. Its behavior was quite different from that of the inorganic acids in that it was extracted in excess of the requirements for protonation of DPPM. Since Cr(VI) extractions were not very satisfactory from this acid it was not examined in detail. However, the solubility of acetic acid in the organic diluents probably accounts for the excess acid determined in the organic phase.

The extractions of HCl by DPPM/diluents were investigated in some detail. Not only were different diluents used but different extraction ratios were employed both in the presence and absence of any Cr(VI). The HCl, Cl^-, and DPPM concentrations were varied. Of the diluents listed in Table 3.1 only those which could be classified as acidic and capable of participation in hydrogen bonding were found to be effective in the extraction of HCl or Cr(VI) and examined further. In agreement with Warnqvist's results[142], the extraction of HCl was negligible in the selected diluents in the absence of DPPM, at least up

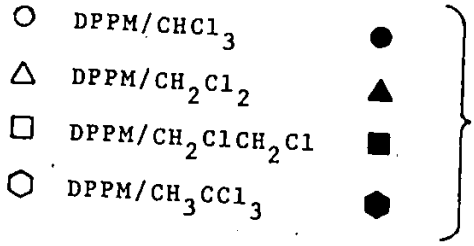
to 6M in acid. Thus, when acid was found in the organic phase it was attributed to the formation of an ion-pair with DPPM, represented as $\overline{\text{DPPMHCl}}$.

One illustration of the effect of the HCl concentration on the extractibility of the acid is represented in Figure 4.2. In all cases 5 mL of the aqueous solution, sometimes containing a $^{51}Cr(VI)$ tracer, were mixed with 2 mL of the 0.10M DPPM/diluent. It can be seen that DPPM is not protonated in CH_3CCl_3 and the small amount of acid determined probably represents only a slight acidity of this diluent. However, in CH_2ClCH_2Cl the organic phase acid content increases with an increase in the HCl concentration until slightly more than 50% of the original DPPM is protonated. Even beyond the range of this diagram, and up to 4.8 M in HCl, little more acid is extracted. In both $CHCl_3$ and CH_2Cl_2 the data suggests that protonation of the DPPM is much more significant. Clearly, trace amounts of Cr(VI) do not change the acid equilibrium situation. Nevertheless, these diagrams must be considered incomplete, for while they depict the extent to which $\overline{\text{DPPMHCl}}$ forms, they do not account for all of the initial DPPM in a system.

A more complete picture may be gained by an examination of the data in Table 4.2 and Figure 4.3. After an extraction had been performed with equal volumes of aqueous HCl and 0.10M DPPM/diluent the total acid concentration in each phase was determined. The DPPM content in the aqueous phase, probably all in a protonated form, was found by the $HClO_4$ extraction technique. The difference between the total acid concentration in the aqueous phase and that attributed to the DPPM represents the true HCl equilibrium concentration. Any DPPM unaccounted

Figure 4.2

The acid concentration in the organic phase after equilibration of 0.10 M DPPM/diluent with various aqueous HCl solutions at an extraction ratio $V/\overline{V} = 5/2$.



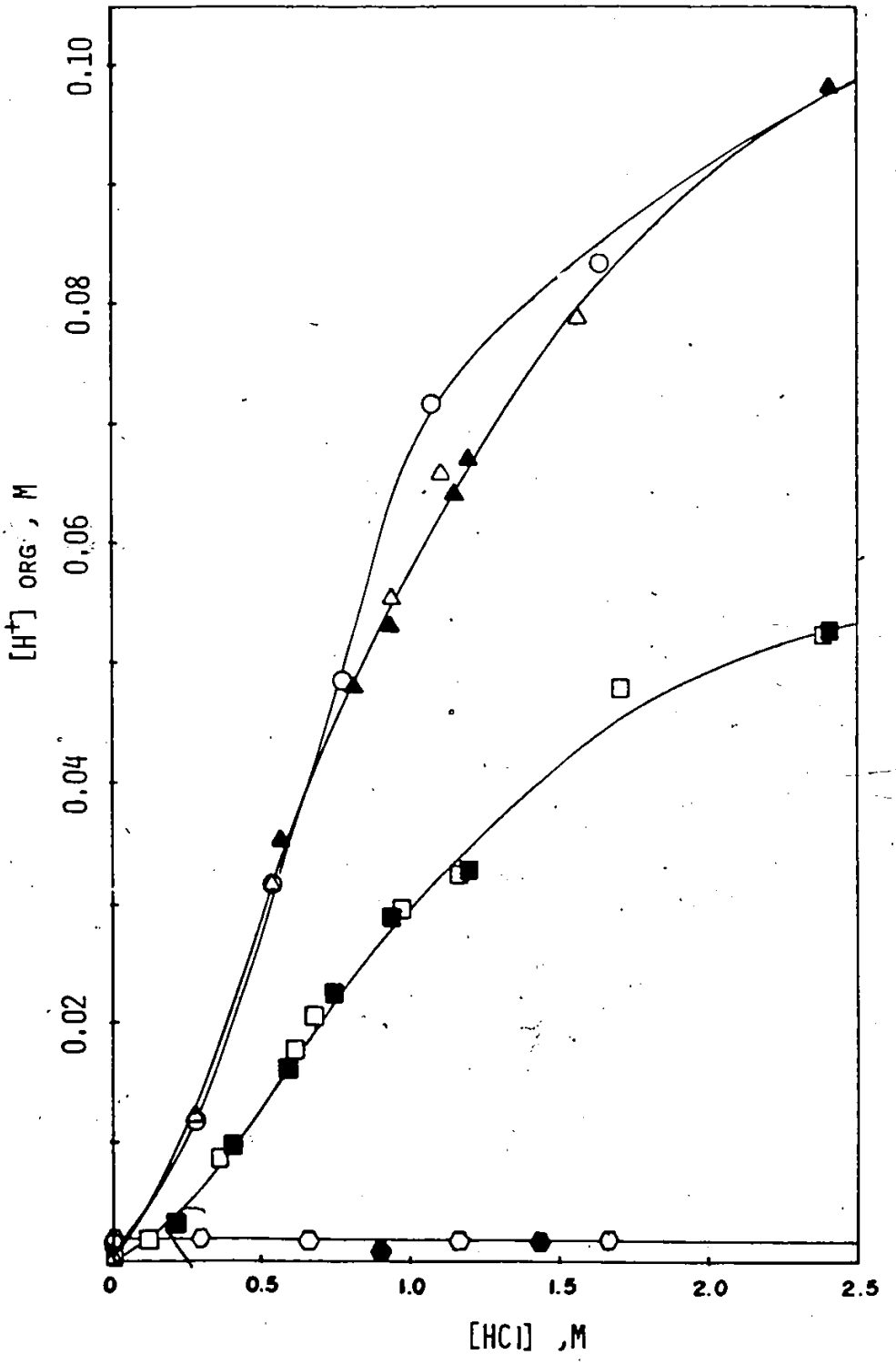

0.10
0.08
0.06
0.04
0.02
[H+] ORG , M
0
0.5
1.0
1.5
2.0
2.5
[HCl] ,M

TABLE 4.2

Concentration of species (M) in an equilibrium mixture of 0.100 M DPPM/diluent and an equal volume of aqueous HCl.

a). CH_2Cl_2 diluent.

[Acid](total)	$[DPPMH^+ + DPPM\ HCl]$	[HCl] equil.	$\overline{[DPPM\ HCl]}$	$\overline{[DPPM]}$
0.179	0.00368	0.175	0.0059	0.0904
0.749	0.00905	0.740	0.0540	0.0370
0.866	0.00919	0.857	0.0585	0.0323
1.714	0.00899	1.705	0.0825	0.0085
4.612	0.00853	4.603	0.0897	0.0018

b) CH_2ClCH_2Cl diluent.

[Acid] total	$[DPPMH^+ + DPPM\ HCl]$	[HCl] equil.	$\overline{[DPPM\ HCl]}$	$\overline{[DPPM]}$
0.118	0.00347	0.115	0.00173	0.0948
0.352	0.01088	0.341	0.00869	0.0804
0.577	0.01716	0.560	0.01976	0.0631
0.802	0.02213	0.781	0.03073	0.0471
1.142	0.02475	1.117	0.04714	0.0281
1.314	0.02428	1.290	0.05494	0.0208
2.172	0.02527	2.147	0.06948	0.0053
4.804	0.02673	4.777	0.07024	0.0030

Figure 4.3

a) The distribution of protonated DPPM after mixing equal volumes of 0.100 M DPPM/CH_2Cl_2 with aqueous hydrochloric acid as a function of the equilibrium acid concentration.

△ in the organic phase

▲ in the aqueous phase

b) The distribution of protonated DPPM after mixing equal volumes of 0.100 M DPPM/CH_2ClCH_2Cl with aqueous hydrochloric acid as a function of the equilibrium acid concentration.

□ in the organic phase

■ in the aqueous phase

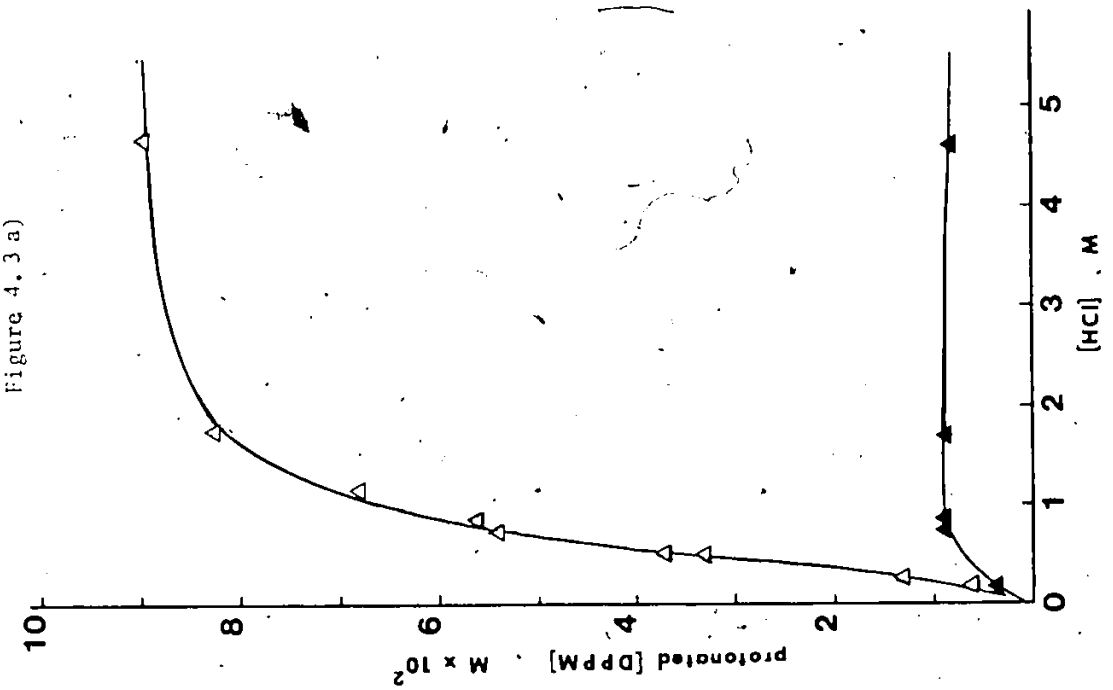


Figure 4.3 a)

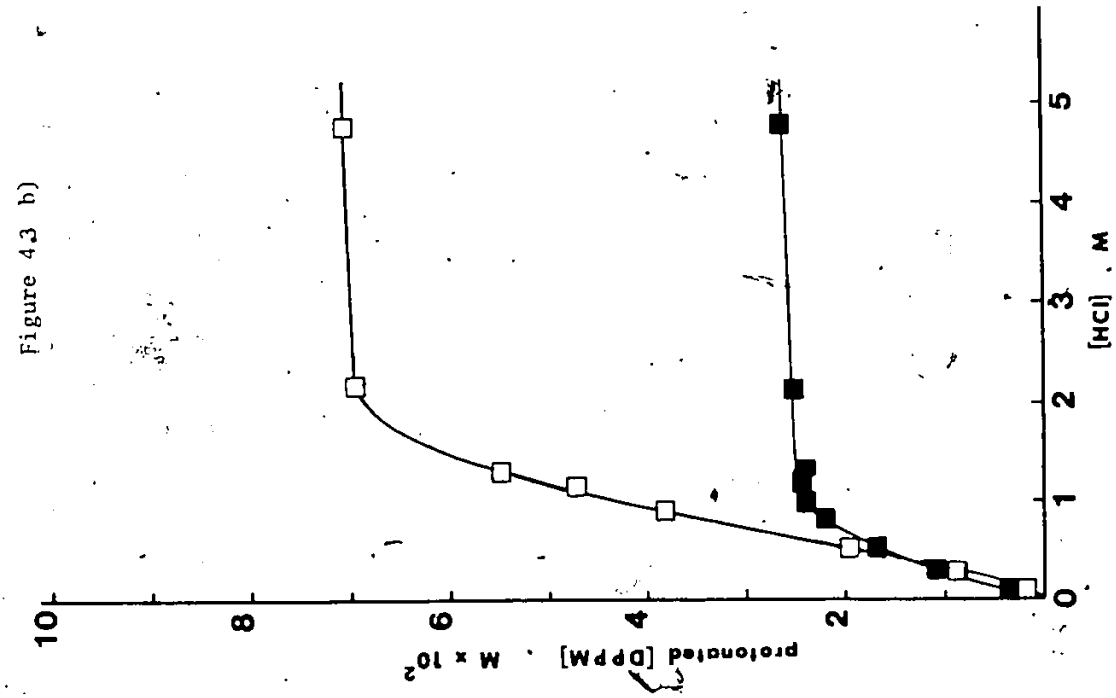


Figure 4.3 b)

for must have remained as a molecular species in the organic phase. The concentrations of the various species, recorded to one digit beyond significance, are with the important diluents CH_2Cl_2, Table 4.2a), and CH_2ClCH_2Cl, Table 4.2b). It is more obvious from the respective Figures 4.3a) and 4.3b) that there are differences between the two diluents. Already noted in Figure 4.2, and confirmed here, is the fact that with CH_2Cl_2 the HCl is more readily extracted. However, there is little difference in the total DPPM protonation for with CH_2ClCH_2Cl a greater proportion of the DPPM appears in the aqueous phase where it is surely protonated. This availability of more extractant in the aqueous phase could have important implications when other anions are available to "exchange" pairing sites with the Cl^- anion of any ion-pair. If the new ion-pair is more aquaphobic it could be more readily extracted than the DPPMHCl.

The extent of acid extraction was examined when the aqueous chloride concentration was changed at a fixed initial concentration of HCl. Since the protonation in the organic phase can occur only if a counter anion is extracted at the same time one would expect that the addition of Cl^- would promote this process. Selected results are recorded in Table 4.3.

Indeed, the addition of Cl^- does lead to enhanced protonation of DPPM. In the 1M acid concentration region the addition of Cl^- to a DPPM/$CHCl_3$ system is about as effective as is the addition of HCl. In fact, the amount of DPPM in the aqueous phase has already been optimized in 1M HCl solutions and the Cl^- added as a salt is even more effective than HCl itself in forcing the protonated DPPM complex into the $CHCl_3$

TABLE 4.3

The effect of the addition of Cl^-, as LiCl, on the equilibrium concentration (M) of species present in a mixture of equal volumes of an aqueous HCl solution and DPPM/diluent.

a). 0.101 M DPPM/$CHCl_3$

$[H^+]$	$[Cl^-]$	$[\overline{DPPM\ HCl}]$	$[DPPMH^+ + DPPMHCl]$	$[\overline{DPPM}]$
1.074	1.074	0.0682	0.0071	0.0257
1.067	2.007	0.0820	0.0048	0.0143
0.987	2.857	0.0938	0.0056	0.0016
1.045	3.855	0.0980	0.0029	0.0001

b). 0.100 M DPPM/CH_2ClCH_2Cl

$[H^+]$	$[Cl^-]$	$[\overline{DPPM\ HCl}]$	$[DPPMH^+ + DPPM\ HCl]$	$[\overline{DPPM}]$
0.277	0.277	0.00739	0.01023	0.0824
0.272	0.761	0.01275	0.00941	0.0788
0.266	1.217	0.01919	0.00951	0.0713

phase. However, at the lower HCl concentration examined in the DPPM/CH_2ClCH_2Cl extraction the protonation of DPPM is further from being optimized (See Figure 4.3b)). Addition of Cl^- as a salt does increase the total protonation of the DPPM but not nearly as effectively as does the addition of HCl which provides for both the H^+ and Cl^- ions.

Varying the initial DPPM concentration in an extraction system provides yet another perspective on the extraction of HCl in the different diluents. In Figure 4.4 the concentrations of protonated DPPM in both the organic and aqueous phase are represented for two different systems. Again it is apparent that the acid extraction is much more complete in CH_2Cl_2 than in CH_2ClCH_2Cl while at the same time there is less DPPM in the aqueous phase. The excellent linearity exhibited would suggest that the determinations are reliable over a wide range of concentrations of DPPM in each phase. Further, the slopes are an indication of the extent of protonation. Of the original $\overline{DPPM}$, Figure 4.4a) depicts 69% as $\overline{DPPMHCl}$ in CH_2Cl_2 and Figure 4.4b) depicts 41% as $\overline{DPPMHCl}$ in CH_2ClCH_2Cl. From Figures 4.3a) and 4.3b) it is obvious that further protonation is possible at higher HCl concentrations but these values do correspond to the concentrations expected by interpolation. However, near 1M HCl the amount of DPPM found in the aqueous phase is close to the maximum in each case as depicted in Figures 4.3a) and 4.3b). In CH_2Cl_2 about 9% of the DPPM is in the aqueous phase according to the slope and in CH_2ClCH_2Cl the respective value is 25%.

The data collected from these experiments may be used to check the assumption that HCl is extracted to form a stable ion-pair in the organic phase. As explained in Section 2.2, it is possible to plot

Figure 4.4

a) The distribution of protonated DPPM after mixing equal volumes of 1.2 M HCl solution with varying initial concentrations of DPPM in CH_2Cl_2.

○ protonated DPPM in the organic phase

● protonated DPPM in the aqueous phase

b) The distribution of protonated DPPM after mixing equal volumes of 1.0 M HCl solution with varying initial concentrations of DPPM in CH_2ClCH_2Cl.

○ protonated DPPM in the organic phase

● protonated DPPM in the aqueous phase

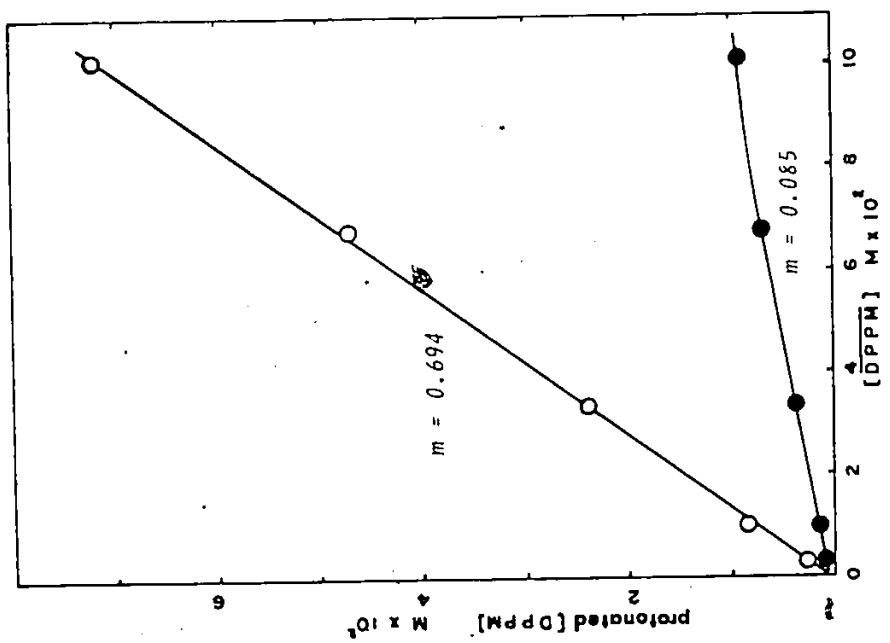


Figure 4.4 a)

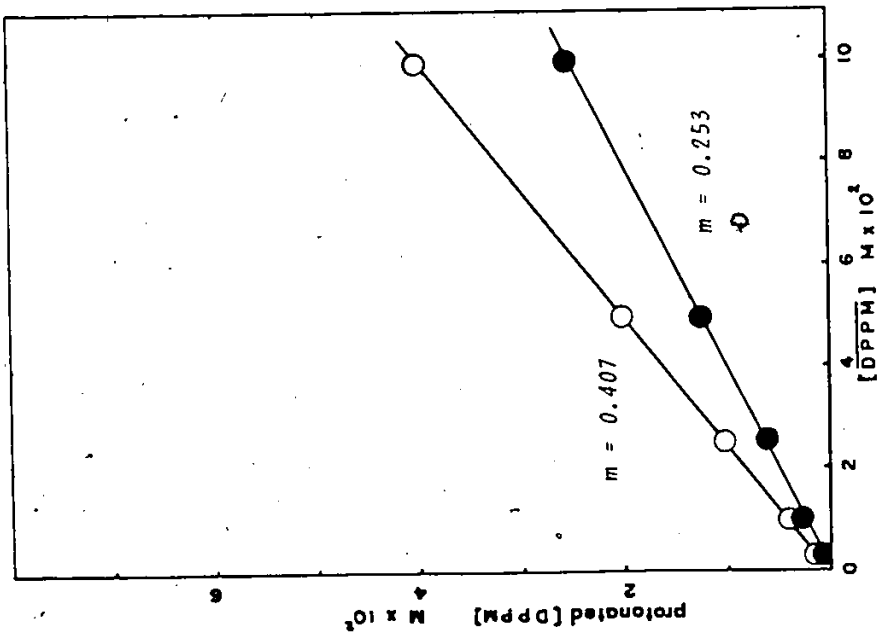


Figure 4.4 b)

$\log[\overline{BH^+A^-}]$ versus $\log\ [\overline{B}] \times a_{HCl}$ to determine the nature of the extracted complex. A plot of $\log\ [\overline{DPPMHCl}]$ versus $\log\ [\overline{DPPM}]\ a_{HCl}$, for the diluent CH_2ClCH_2Cl, is illustrated in Figure 4.5. Although there is some recognizable curvature this would not be unexpected, particularly at each extreme. Since CH_2ClCH_2Cl has the highest dielectric constant of the effective diluents there could be some dissociation of the ion-pair, $\overline{DPPMH^+Cl^-}$, at extremely low concentrations. At the highest concentration range there is generally a non-linearity in these kinds of plots.[112,118] Diamond[118] suggests that this may be caused by activity or solubility effects, which cannot be accounted for, rather than any polymerization. On the other hand, the most important working region for the extractions of interest is represented by the middle region of Figure 4.5. Here the slope of the curve is very close to one, a clear indication that the ion-pair is very stable and may be accurately represented as $\overline{DPPMHCl}$.

The concentration of protonated DPPM in each of the diluents is indeed an equilibrium concentration. It is achieved rapidly, certainly within 10 seconds in a mechanical mixing system, and remains constant over an extended period of time. For instance, there is no change in acidity in a CH_2Cl_2 diluent system, when stored as the separated organic phase or in contact with the acid, for a period of 3 months.

4.2.2 The extraction of Cr(VI)

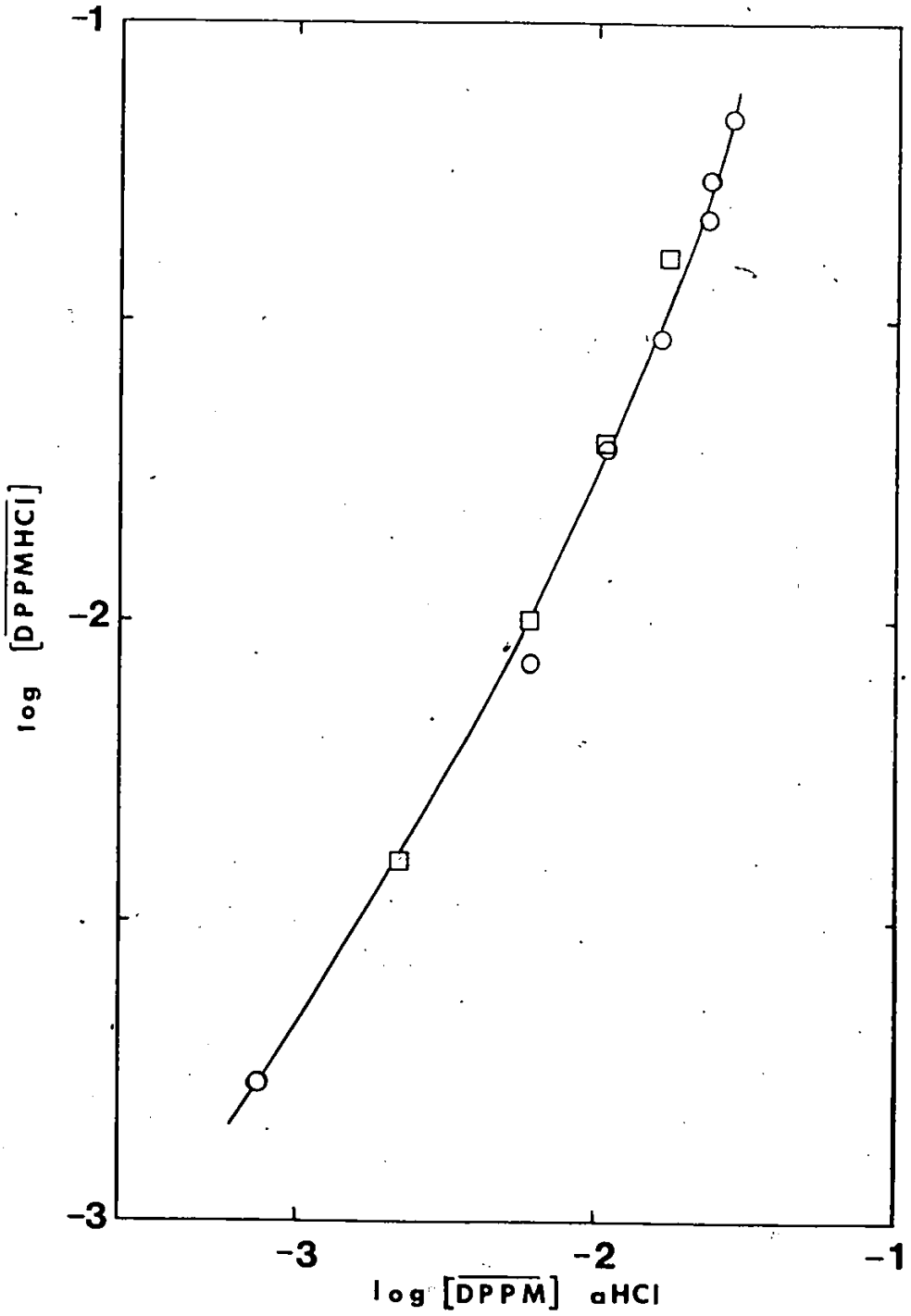
Iqbal and Ejaz[74] have reported that $HCrO_4^-$ is extracted by $DPPM/CHCl_3$ from acidic solutions to an extent which varies not only with

Figure 4.5

The concentration of DPPM in CH_2ClCH_2Cl as a function of the product of the concentration of molecular DPPM and the activity of HCl.

○ Determination at a fixed initial 0.1 M DPPM/CH_2ClCH_2Cl and variable concentrations of HCl.

□ Determination at a fixed initial 1.0 M HCl and variable concentrations of DPPM/CH_2ClCH_2Cl.


-1
-2
-3
log [DPPMHCl]
-3
-2
-1
log [DPPM] aHCl

the acid and DPPM concentration but also with the Cr(VI) concentration. Since with their extractions from HCl solutions the log D versus log DPPM plot was a straight line with a slope of one the Cr(VI) must be extracted by DPPM on a one to one basis. They suggested that the complex formed was the ion-pair $DPPMH^+$ $HCrO_4^-$. There is no disagreement with their data but the interpretation is suspect. An examination of Table 2.1 and other reports[158,159] indicates that CrO_3Cl^- could be considered as an extractable species as well as $HCrO_4^-$. Further, the reduction problems experienced with Cr(VI) at trace concentrations should not be overlooked. The lower value for the distribution ratio, D, when Cr(VI) was at trace concentrations may relate to a reduction phenomenon not recognized by Iqbal and Ejaz.

It was concluded from initial investigations that there was indeed a problem with reduction when examining the extraction system. While the extracted chromium, placed initially in the aqueous phase as $^{51}Cr(VI)$, was totally anionic according to non-aqueous ion-exchange procedures, most of the ^{51}Cr activity in the aqueous phase after extraction was in the form of Cr(III). The proportion of the activity found in the cationic form varied considerably. Both the initial Cr(VI) concentration and extraction conditions imposed upon the system influenced the extent of reduction, and thus the distribution ratio.

In the Cr(VI) extractions, reduction was most significant at the lowest Cr(VI) concentrations, in agreement with results in the aqueous phase alone. This was reflected in the range of distribution values from near D=3 at 1 ppb Cr(VI) to near D=30 at 1×10^{-3} M Cr(VI). With trace levels, the preparation time, when Cr(VI) could be in contact with

the HCl, could be crucial. Even the mixing method and the length of time for mixing or sitting after extraction but before performing a radioassay could influence the distribution ratio because of the reduction phenomena.

Clearly the extraction procedure had to be standardized. While rapid mechanical mixing followed by centrifugation and prompt assay were possible and preferable under laboratory conditions these were ideals which would be difficult to achieve under many sampling conditions. The procedure that was adopted involved a manual extraction with an equilibration time of three minutes. Although one minute was an adequate mixing time when the extraction ratio was 1:1, when the extraction ratio approached 15:1 it was found that the distribution ratio was maximized in three minutes. Mixing for five or more minutes led to a marginal increase in the Cr(VI) reduction. After mixing the two phases were allowed to separate by gravity for two minutes. An aliquot of solution from each phase was then assayed for γ-activity. Separations were clean when using 2 mL of DPPM/$CHCl_3$ and up to 50 mL of the aqueous phase. Thereafter, because of surface, phase separation or solubility problems it was difficult to get a 1 mL aliquot of the organic phase from the aqueous phase of more than 50 mL. Although commonly employed for convenience, centrifugation was not required as long as the extraction ratio was not too great or the mixing too vigorous.

To gain an understanding of the DPPM/$CHCl_3$ extraction unencumbered by any reduction problem the use of Ce(IV) to oxidatively stabilize the Cr(VI) was explored. In keeping with the results

mentioned for the oxidation of Cr(III) in aqueous solutions it was found that 1×10^{-3} M Ce(IV) introduced into the aqueous phase of an extraction system was more than adequate to stabilize Cr(VI) at trace concentrations.

The results for the extraction of oxidatively stabilized Cr(VI) from HCl solutions by 0.1M DPPM/$CHCl_3$ at an extraction ratio near 25:2 are listed in Table 4.4. In Figure 4.6 the relationship between the distribution ratio, D, and the acid concentration is depicted in an expanded form for the acid concentrations between 0.5 and 1.5M HCl. Figure 4.7 is a more conventional extraction curve. It can be seen that with oxidatively stabilized Cr(VI) there is no difference in the distribution ratio at a concentration of Cr(VI) from less than 1 ppb to 2 ppm. However, in the absence of Ce(IV) the distribution ratio is smaller, with the decrease in D from the stabilized counterpart being greatest for the sample of lowest concentration. An ion-exchange analysis confirmed that the ^{51}Cr activity not in the organic phase is essentially as Cr(III) so that the decrease in D can be attributed primarily to a reduction problem.

From Figure 4.7, which, for the sake of clarity, includes few of the data points depicted in Figure 4.6, it is obvious that the extraction of chromium changes as there is a change in the HCl concentration. D initially increases but reaches a maximum near 1M HCl to be followed by a rapid decline at high acidities.

An analytical procedure involving this extraction and AAS chromium detection in the organic phase was investigated and found viable (Section 4.2.6). However, the distribution ratio in $CHCl_3$ was

TABLE 4.4

Extraction of $^{51}Cr(VI)$ from HCl solutions by 0.10 M DPPM/$CHCl_3$. Mixing times 3 minutes.

	[HCl]	log [HCl]	D	log D
a). Cr(VI) < 0.1 ppb, Ce(IV) = 5 x 10^{-4}M, $V/\bar{V}$ = 25/2				
	0.12	-0.921	0.64±0.05	-0.194
	0.58	-0.237	14.0±0.5	1.147
	0.60	-0.221	15.9±0.8	1.202
	0.84	-0.076	26.6±0.5	1.426
	0.89	-0.050	28.9±1.6	1.460
	1.05	0.022	31.8±1.8	1.502
	1.17	0.068	31.6±2.0	1.500
	1.20	0.080	33.7±2.0	1.528
	1.48	0.169	17.4±0.9	1.239
	2.00	0.302	4.6±0.2	0.660
	2.41	0.381	2.2±0.1	0.336
b). Cr(VI) < 0.1 ppb, no Ce(IV)				
	0.84	-0.074	20.9±0.4	1.319
c). Cr(VI) = 2 ppm, Ce(IV)=5 x 10^{-4}M, $V/\bar{V}$ = 28/2				
	0.84	-0.076	26.6±0.5	1.423
	0.89	-0.051	27.5±2.0	1.439
	0.99	-0.004	29.4±1.7	1.469
	1.09	0.038	31.5±2.5	1.498
	1.29	0.109	21.8±1.6	1.338
d). Cr(VI) = 2 ppm, no Ce(IV)				
	0.84	-0.074	24.1±0.4	1.383

Figure 4.6

Extraction curve for Cr(VI) from 0.5 to 1.5 M HCl solutions by 0.10 M DPPM/$CHCl_3$.

○ Cr(VI) < 0.1 ppb, stabilized by Ce(IV).
◇ Cr(VI) = 2 ppm, stabilized by Ce(IV).
● Cr(VI) < 0.1 ppb.
◆ Cr(VI) = 2 ppm.

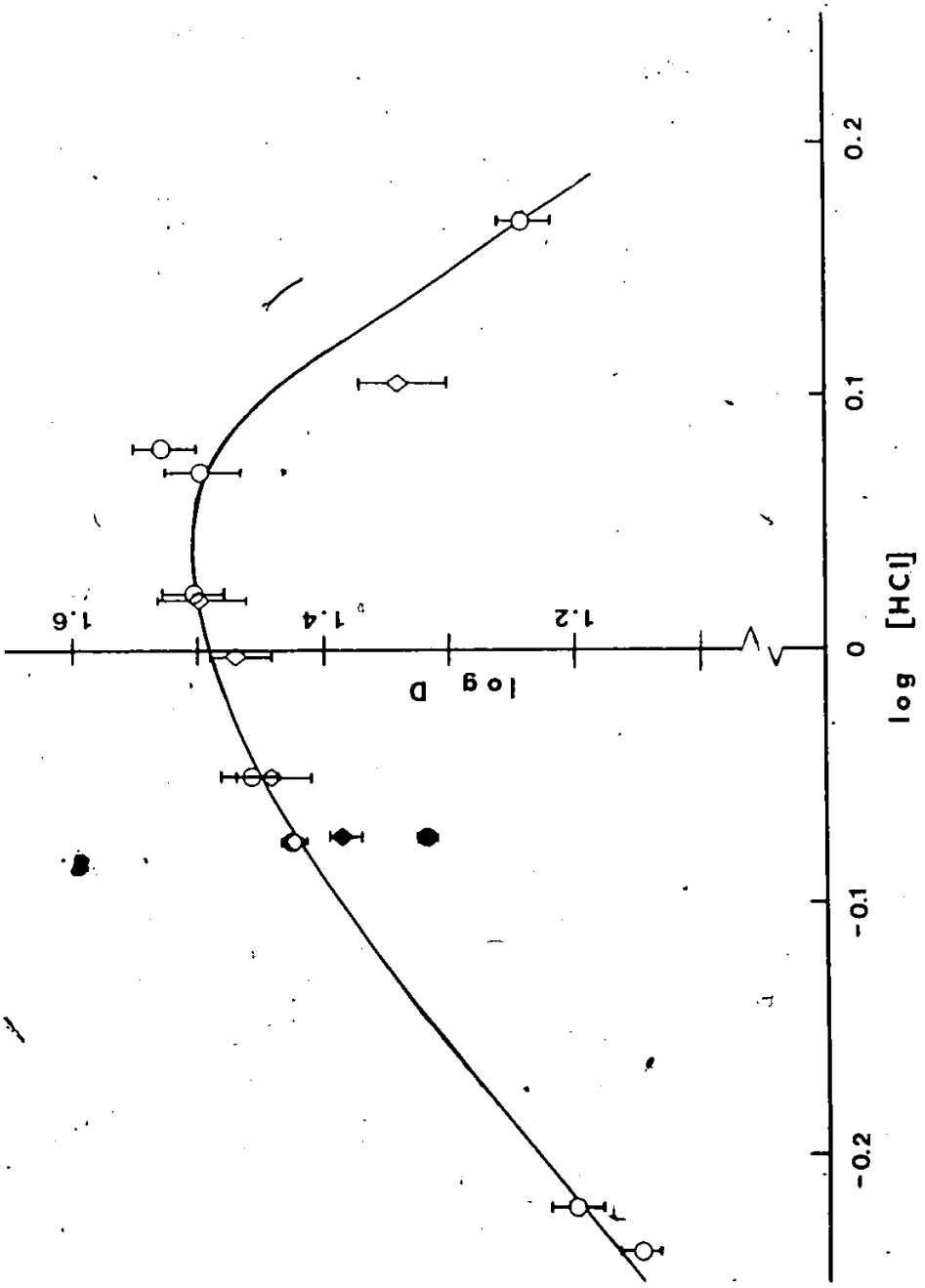
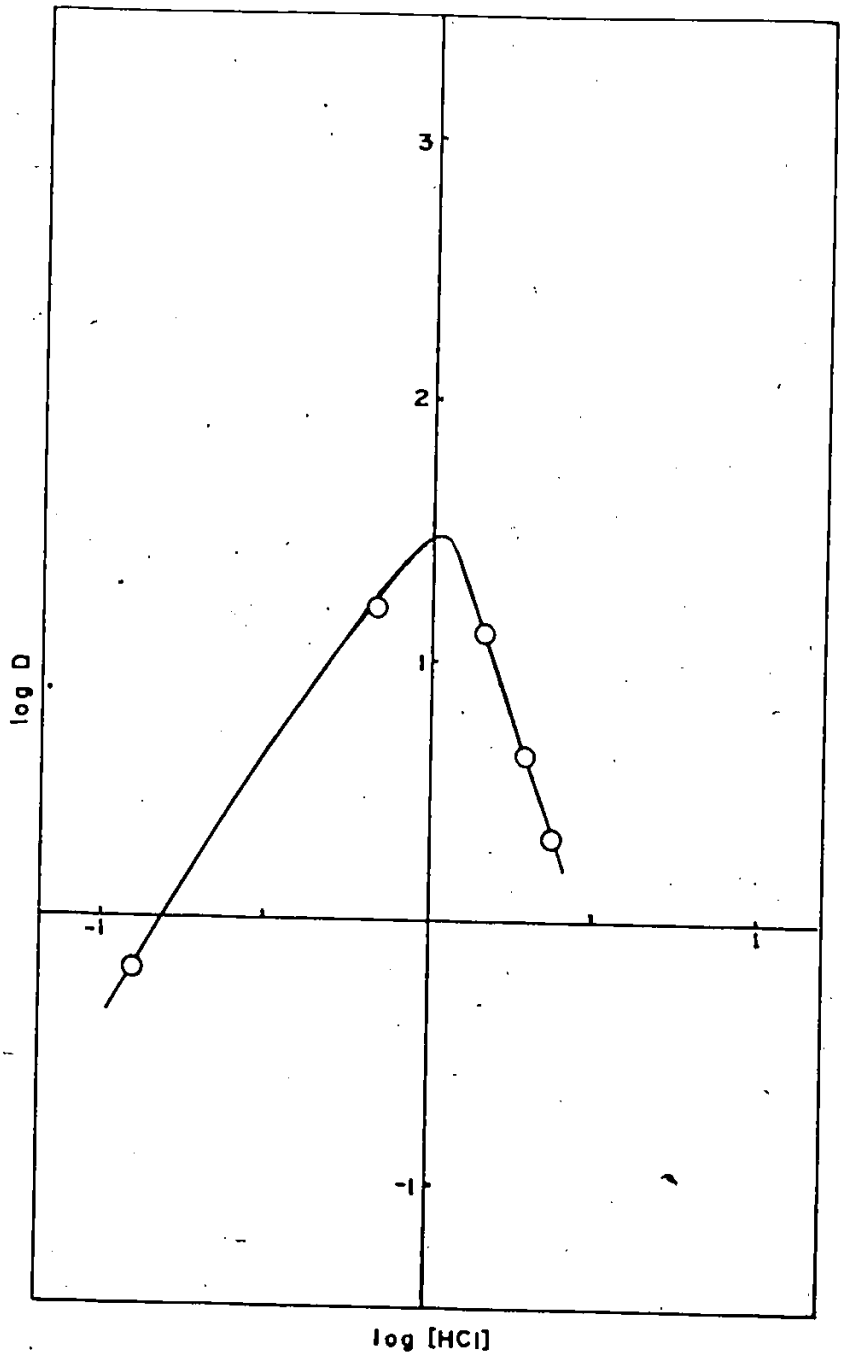

log D
1.2
1.4
1.6
0
0.1
0.2
-0.1
-0.2
log [HCl]

Figure 4.7

Extraction curve for Cr(VI) from HCl solutions by 0.10 M DPPM/$CHCl_3$.


3
2
1
-1
1
-1
log D
log [HCl]

not as high as desired for trace investigations and there was a problem of both poorer and irreproducible distribution ratios with little change in the solution if it was not oxidatively stabilized. System modification seemed worth exploring, particularly the effect of a change of diluent.

There is a dramatic diluent effect in the extraction of Cr(VI) from aqueous HCl solutions into 0.10M DPPM/diluent. While the extractions using a number of diluents were checked there was no thorough investigation unless the system proved to be at least as effective as it was with $CHCl_3$. Table 4.5 lists the approximate distribution ratio maxima, all of which are from solutions which are near 1M in HCl. The extraction curves are also illustrated for several of the diluents with the highest dielectric constants of the diluents investigated: Figure 4.7 for $CHCl_3$, Figure 4.8 for CH_2Cl_2 and Figure 4.9 for CH_2ClCH_2Cl and CH_3CCl_3.

It is immediately apparent that the effect caused by the diluent change is due to a specific interaction rather than just a difference in the dielectric constant or dipole moment (Table 3.1). For example, the dielectric constant of CH_3CCl_3 is close to that of CH_2Cl_2, and its dipole moment is even greater than that of CH_2Cl_2. Yet, extraction of Cr(VI) is two orders of magnitude poorer. Ether and chloroform have similar dielectric constants and dipole moments but in chloroform the extraction of Cr(VI) is much more efficient. Freon 11 differs from chloroform only in the substitution of a fluorine atom for a hydrogen atom, yet the Cr(VI) extraction in freon is barely measurable. All of these facts suggest that it is the potential for hydrogen bonding of the

TABLE 4.5

The extraction of Cr(VI) by 0.10 M DPPM/diluent. The distribution ratio for Cr(VI), D, is recorded for the approximate range of acid concentrations in which the extraction is maximized from Ce(IV) stabilized HCl solution.

Diluent	Acid Concentration M	distribution ratio Cr(VI) D
$CHCl_3$	1.1 ± 0.1	32 ± 2
CCl_4	1 ± 0.1	$<10^{-3}$
$CFCl_3$	0.8 ± 0.4	$<10^{-2}$
CH_2Cl_2	0.9 ± 0.1	300 ± 50
CH_2ClCH_2Cl	0.8 ± 0.2	700 ± 100
CH_3CCl_3	1.0 ± 0.1	3.0 ± 0.2
$CHCl = CCl_2$	1.2 ± 0.2	2.2 ± 0.2
$CH_3CH_2OCH_2CH_3$	1.0 ± 0.1	1.2 ± 0.2

Figure 4.8

Extraction curve for Cr(VI) from HCl solutions by:

△ 0.10 M DPPM/CH_2Cl_2

▲ 0.01 M DPPM/CH_2Cl_2

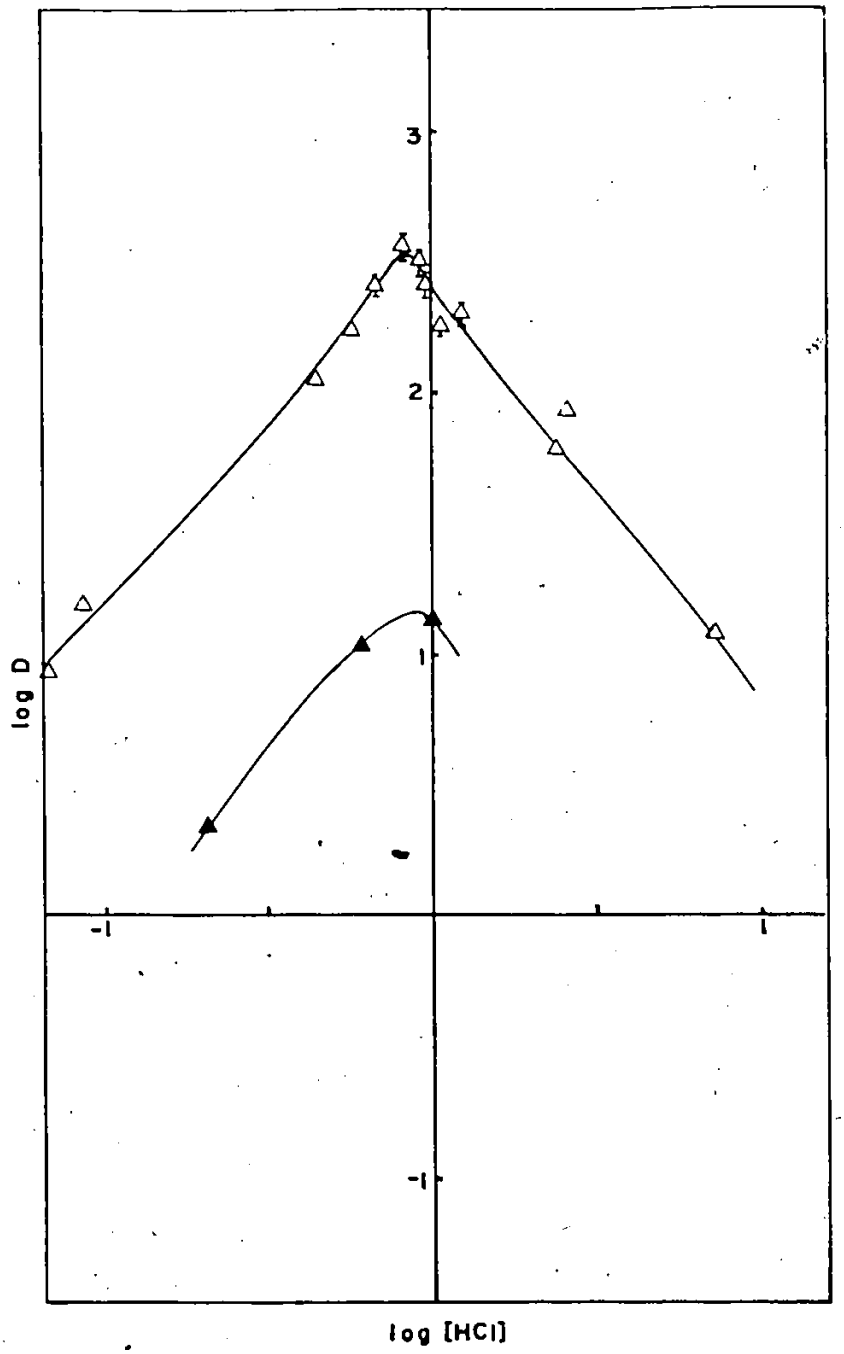
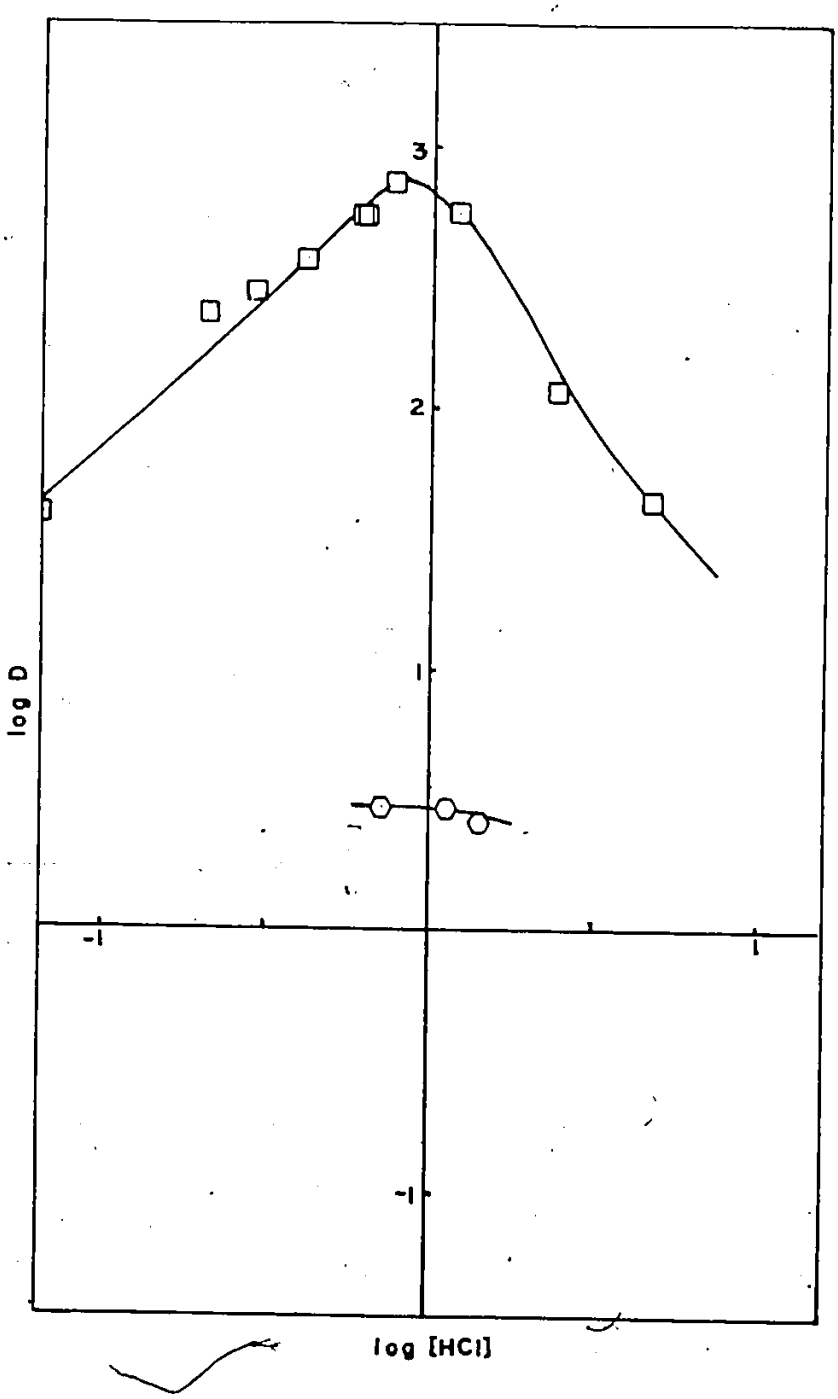

3
2
1
-1
1
-1
log D
log [HCl]

Figure 4.9

Extraction curve for Cr(VI) from HCl solutions by:

□ 0.10 M DPPM/CH_2ClCH_2Cl

○ 0.10 M DPPM/CH_3CCl_3


3
2
1
-1
log D
-1
1
log [HCl]

diluent that determines whether or not it is in a class of organic solvents which enhance Cr(VI) extractions with DPPM.

Within the series $CHCl_3$, CH_2Cl_2 and CH_2ClCH_2Cl, an increase in the dielectric constant seems to increase the Cr(VI) extraction efficiency. However, the extraction of Cr(VI) cannot be considered separately from other aspects of the system. As was demonstrated in Section 4.2.1, diluent effects on the protonation and distribution of DPPM are significant. Thus, it is the overall influence of the diluent on the total system, arising in part from factors other than just the dielectric constant, which dictates the value of the distribution ratio for Cr(VI).

In Figure 4.8 the effect of a change in the DPPM concentration in CH_2Cl_2 is illustrated. This is exactly as expected from the comparable results with the $CHCl_3$ diluent.[74] It is consistent with the extraction of a reasonably stable ion-pair over the acid concentration range examined.

Extractions from other acids were next considered. It is known that the Cr(VI) extraction curves from HNO_3 and H_2SO_4 solutions, when using the 0.10M DPPM/$CHCl_3$ extraction system, are almost identical and illustrate the fact that the extractions are not effective.[74] However, by changing the diluent to CH_2Cl_2 marked differences between the two acids become apparent. From 1M HNO_3 extraction of Cr(VI) is still not appreciable, D = 0.16 ± 0.01, but from 1M H_2SO_4 the value is D = 8.9 ± 0.3. Although the distribution ratios are much lower than from HCl solutions, it is no longer possible to lump extractions from both of these acids together and suggest that they are not effective "due to the

very large hydrophilic tendency of the hydrogen sulfate and nitrate ions".[74] Rather, it seems more probable that the extraction from HNO_3 is limited by two factors - the Cr(VI) complex existing in HNO_3 solutions may not be the most favorable for ion-pair formation with $DPPMH^+$ and the NO_3^- competes vigorously for the pairing sites and is readily extracted, just as it was in the absence of Cr(VI). On the other hand, protonation of DPPM and extraction of SO_4^{2-} or HSO_4^- into the organic phase is known to be poor. Thus, either the problem of forming the protonated extractant and providing for its proper distribution so that the Cr(VI) anion can form an extractable ion-pair is the impediment or again, the Cr(VI) complex in H_2SO_4 does not create as extractable an ion-pair as the Cr(VI) complex found in HCl solutions.

The fact that Cr(VI) could be extracted from H_2SO_4 solutions when using as diluent CH_2Cl_2 or CH_2ClCH_2Cl provided an opportunity to check whether or not the complex extracted was a simple ion-pair as extracted from HCl solutions. The plot of log D versus log DPPM (Figure 4.10) for an extraction from 0.54M H_2SO_4 by 0.10M DPPM/CH_2ClCH_2Cl when the Cr(VI) concentration was 3×10^{-3} M suggests that the ion-pair is not one in which the protonated DPPM combined with a single mononegative anion containing but one Cr atom. It is apparent that from H_2SO_4 solutions the Cr(VI) extracted is of a mixed type, at least in this system which was checked.

Further evidence for the different extraction behavior from H_2SO_4 solutions was uncovered when the protonation of DPPM was examined for this extraction in the presence of 3×10^{-3} M Cr(VI) and it was compared to the situation with H_2SO_4 alone (Figure 4.11). Remember that

Figure 4.10

The variation in the distribution ratio of 3×10^{-3}M Cr(VI) with the concentration of DPPM in CH_2ClCH_2Cl from a 0.54 M H_2SO_4 solution.

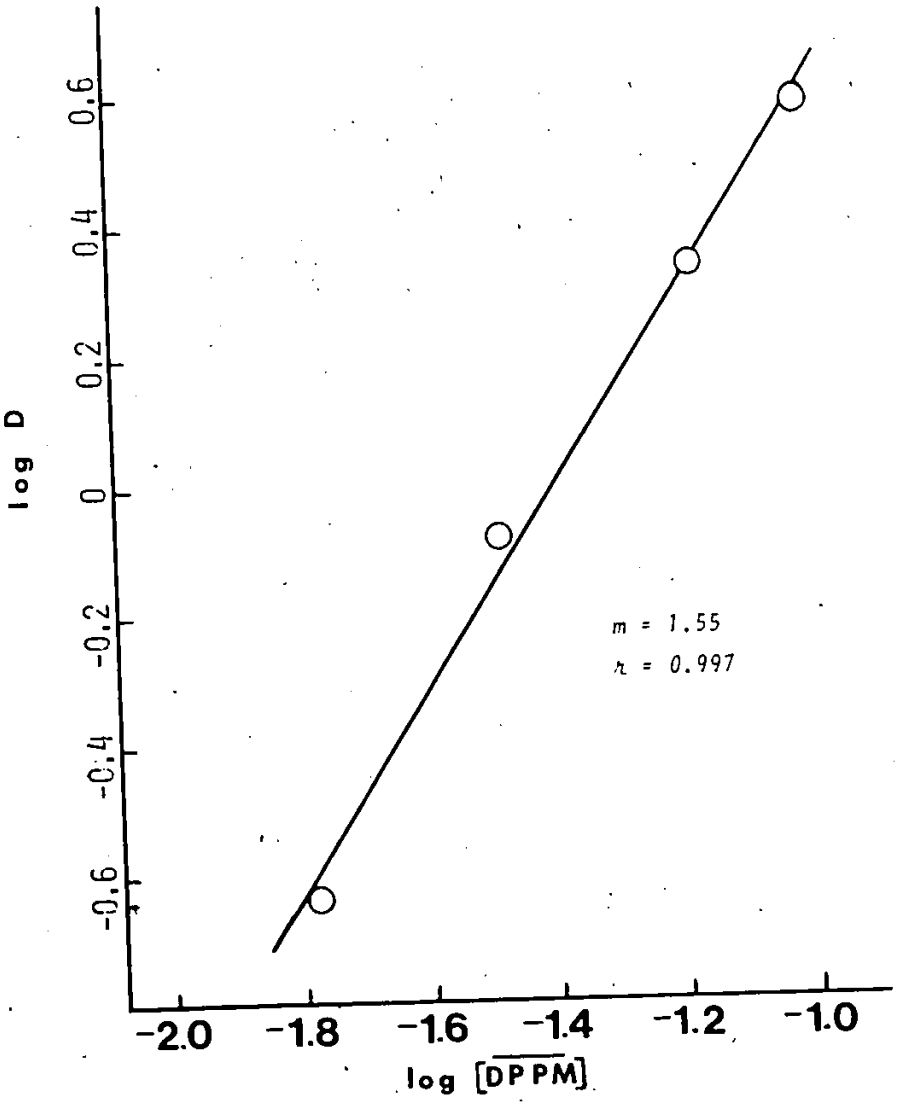

log D
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-2.0
-1.8
-1.6
-1.4
-1.2
-1.0
log [DPPM]
m = 1.55
r = 0.997

Figure 4.11

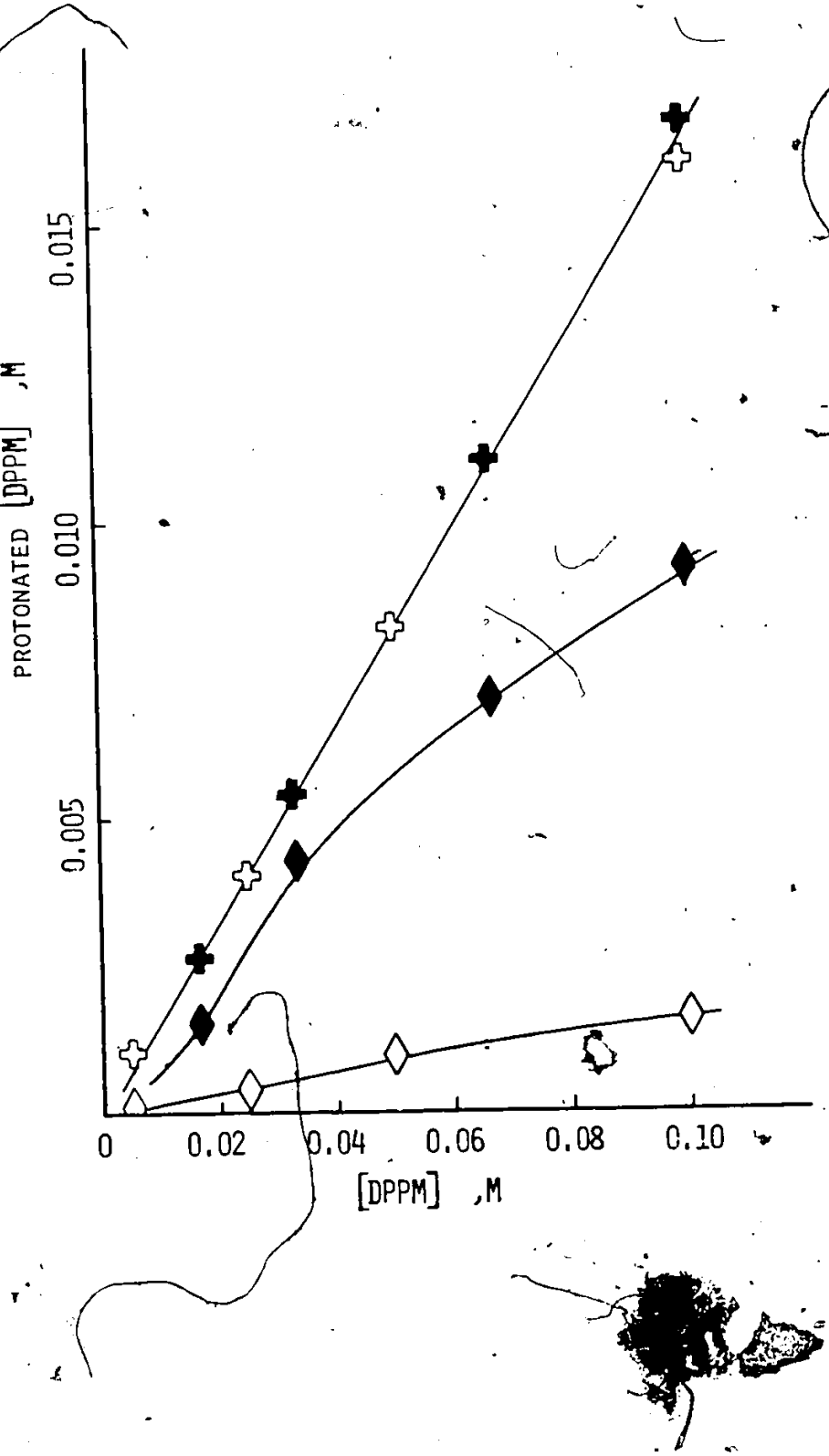
The distribution of protonated DPPM after mixing equal volumes of 0.54 M H_2SO_4 with varying initial concentrations of DPPM/CH_2ClCH_2Cl:


aqueous phase protonation for pure H_2SO_4


aqueous phase protonation in the presence of 3×10^{-3}M Cr(VI) in H_2SO_4


organic phase protonation for pure H_2SO_4


organic phase protonation in the presence of 3×10^{-3}M Cr(VI) in H_2SO_4


PROTONATED [DPPM] ,M
0.015
0.010
0.005
0
0.02
0.04
0.06
0.08
0.10
[DPPM] ,M

the total protonation of DPPM when H_2SO_4 is used is less than when HCl is used, and the distribution of the protonated species favors the aqueous rather than the organic phase. A comparison of Figure 4.11 and Figure 4.4b) would be in order. In the presence of this Cr(VI) the total protonation increased. However, there was a negligible change in the aqueous phase but a marked alteration in the organic phase. Since it is unlikely that the H_2SO_4 itself would be extracted in a substantially different way in these two cases it seems probable that the acidity in the organic phase can be attributed to the extraction of an acidic Cr(VI) species.

While a very extensive radiotracer examination of the extractions from H_2SO_4 solutions could prove of interest, little additional time was committed because it does not appear likely that such an effort would meet the objective of maximizing the trace extraction of Cr(VI) from aqueous solutions. However, as will be seen, the spectra from such systems were examined when the Cr(VI) concentration was substantially above the ppb region of most interest, primarily to compare these with the better extractions from HCl.

Extraction of Cr(VI) from $HClO_4$ solutions was not good. Even with 0.10M DPPM/CH_2ClCH_2Cl only a value of D = 0.025 was achieved from 0.93M $HClO_4$. The competition for ion-pair formation and extraction when a solution contains such a large concentration of ClO_4^- and but traces of Cr(VI) does not allow for much removal of the Cr(VI) anion which exists in this solution.

The extraction of Cr(VI) from HBr solutions seems to be intermediate between that of HCl and HNO_3, just as was the extraction of

the acid itself. For the system mentioned in that context, using 1.4M HBr and 0.10M DPPM/CH_2ClCH_2Cl, the extraction gave rise to a value of D = 11.9 ± 0.5.

While not an acid which would be chosen for the DPPM/diluent extraction of Cr(VI), acetic acid does exhibit a concentration effect which is somewhat different from that of the inorganic acids. The distribution ratio increases even beyond 1M acid in a fairly systematic manner in a 0.10M DPPM/CH_2ClCH_2Cl extraction.

$[CH_3COOH]$ M	0.26	0.50	1.03	2.04
D	0.06	0.09	0.20	0.42

Because it was not possible to evaluate the protonation of the DPPM in such a system it is difficult to attribute this observation to changes in the extractant or the Cr(VI) complex.

The effect of adding a number of salts to extraction systems was investigated. In agreement with the results published by Iqbal and Ejaz[74], when the extraction of Cr(VI) was from an HCl solution the addition of chloride salts had no depressing effect but rather led to an improved extraction efficiency in some acidity ranges. Using a 0.10M DPPM/$CHCl_3$ system the addition of LiCl to a solution already 1M in HCl increased the distribution ratio. Thus, rather than experiencing a marked decrease in the distribution ratio, D, when both the H^+ and Cl^- concentration are increased simultaneously (Figures 4.6 and 4.7) there was an actual increase to D = 40 at a total Cl^- concentration of 3.86M. A concurrent determination showed that there were also changes in the DPPM protonation and distribution (Table 4.3a) but, obviously, these changes did not impede the extraction. Clearly, the depression of the

Cr(VI) extraction at higher HCl concentrations is due to an interaction of the proton with either the extractant or the Cr(VI) complex in solution.

At lower HCl concentrations the effect of adding a chloride salt is not so clear. In this region below 1M in HCl the distribution ratio is increasing rapidly as the total acid concentration increases with any of the different diluent systems (Figures 4.7, 4.8 and 4.9). The extraction with the 0.10M DPPM/CH_2ClCH_2Cl system exemplifies this situation. With 0.27 M H^+, the Cl^- concentration was increased to 1.22M with little change in the distribution ratio for Cr(VI), D = 260 ± 20. Had both H^+ and Cl^- been increased to the same extent the extraction would have improved considerably. This result should be examined with Tables 4.2b) and 4.3b) in view. It is obvious that the protonation of DPPM increases more rapidly with an increase in the concentration of both H^+ and Cl^- that with Cl^- alone. It is probable that the protonation and distribution of the DPPM are very important in this region. In fact, when adding Cl^- or comparable amount of HCl, the value of the distribution ratio for Cr(VI) may depend more on changes in the extractant than any changes in the Cr(VI) species present initially in the aqueous phase. However, at even slightly higher acid concentrations the addition of Cl^- begins to exert its influence. By adding Cl^- in 0.1M increments to a solution which was 0.4M in HCl the distribution ratio for Cr(VI) increased from 350 ± 30 to 450 ± 40 when the total Cl^- concentration had reached 0.7M.

By adding Cl^- to a solution of an acid other than HCl and then examining the extraction of Cr(VI) an even more dramatic change was

noted. As an illustration; the extraction of Cr(VI) from 0.93M $HClO_4$ by 0.10M DPPM/CH_2ClCH_2Cl has a value of D < 0.025, but when 1.2M HCl is added D = 4.7 and when 1.0M NaCl is added D = 18.6. The ClO_4^- must compete with the Cr(VI) species in the formation of an extractable ion-pair. In the absence of Cl^- the Cr(VI) species cannot compete effectively. However, when HCl is added, even though the total H^+ concentration exceeds 2M, the Cr(VI) is extracted much better. Closer to an H^+ concentration where optimum extraction occur, in the presence of 0.93M H^+ from the $HClO_4$ and 1.0M Cl^- from the chloride salt, the Cr(VI) distribution ratio is greater still. This chloride effect was noted for other acids as well, even acetic acid, but to a lesser extent.

A converse approach, the addition of sulfate, nitrate and perchlorate salts to an HCl solution, was also taken. In agreement with the results published by Iqbal and Ejaz[74], the extraction of Cr(VI) was not changed in the presence of 0.1M sulfate ions but was depressed somewhat by 0.1M nitrate ions. However, the addition of even 0.1M $NaClO_4$ had a significant effect on the distribution ratio. For example, using 0.10M DPPM/CH_2ClCH_2Cl as extractant, addition of 0.1M $NaClO_4$ to 0.8M HCl reduced the value to D = 35. These results can be explained by remembering the extent to which each parent acid of these salts is extracted. Since sulfates, or bisulfates, do not protonate DPPM in the organic phase very well, they are not extracted and would not compete with the Cr(VI) extracted from a solution of HCl. Nitrates would compete with the Cr(VI) anions for association with the protonated DPPM. Perchlorates would complete even more effectively and virtually all of the DPPM would be protonated and ion-paired in the organic phase, the

complex such as $\overline{DPPMHClO_4}$ predominating rather than any Cr(VI) containing complex.

From the description of both the acid and salt effects it seems most probable that the extraction of Cr(VI) from HCl or Cl^- containing solutions is more efficient than that from solutions containing other acids and/or their anions for two reasons:

1) The extractant protonation and distribution between the two phases is most favorable in HCl solutions. The effective availability of the ion-pair DPPMHCl is greater than that of ion-pairs containing different anions from the other acids examined.

2) The Cr(VI) species existing in acidic solutions in the presence of Cl^- can readily displace the Cl^- of the DPPMHCl ion-pair. The resulting ion-pair containing the Cr(VI) must be very aquaphobic and is distributed primarily in the organic phase. In fact, the Cr(VI) species produced in the presence of Cl^- can compete for the pairing sites on the $DPPMH^+$ with the anions of the other acids and is extracted, whereas the Cr(VI) species existing in these acidic solutions alone is not extracted as efficiently.

The stability of the extract with Cr(VI) near a concentration of 1 ppb was examined to determine whether or not it could be stored in this form in case it became necessary to perform a final analysis at a later time. The labelled Cr(VI) extract in 0.10M DPPM/$CHCl_3$ was placed in both sealed glass and polypropylene vials. However, there was considerable swelling of the polypropylene which was attributed to wall penetration by the diluent. Further examinations confirmed that a measurable mass of diluent was picked up by the polypropylene. In the

glass containers sealed with Teflon inserts in screw caps there was no loss of material but it became apparent that there was a gradual redistribution of the activity. The radioactivity of the solution decreased slowly as the container walls adsorbed ^{51}Cr. Within four days approximately 25% of the radiolabel resided on the glass surface rather than in solution. Silanization of the container proved to be of no value and there was even an increase in the wall loss problem.

This loss of chromium from solution with the other diluents was comparable. However, when to the same radiolabelled solution, from which an extract into 0.10M DPPM/CH_2ClCH_2Cl was prepared, there was an addition of $Cr_2O_7^{2-}$ to make the final Cr(VI) concentration about 20 ppm the extract had a much smaller loss of activity in 24 hours. The loss to container walls decreased from about 10% to 3%. With ppb chromium this loss from the organic extract within a few days was confirmed by AAS analysis. In support of the tracer evidence that in the ppm concentration range the extract was more stable, spectral analysis of solutions kept for more than a week indicated that there was negligible loss of absorptivity, although the absorbance maximum shifted from λ = 364 to λ = 354 nm and there was a blurring of the fine structure.

In hopes that this instability problem in the extract could be better understood a series of samples were placed in sealed vials in contact with aqueous solutions of selected characteristics. It was confirmed, as the extraction characteristics dictate, that when the extract containing Cr(VI) was placed in contact with pure water the water became acidic, gaining HCl from the dissociation of the ion-pair originally in the organic phase, and nearly all of the chromium ended up

in the aqueous phase. However, in the presence of HCl solutions the distribution in the organic phase should be favored. Further, adsorption of chromium by the container walls should be suppressed in the presence of acid and not only could the loss of chromium from the organic extract be readily monitored but also it could be determined whether it appeared as Cr(III) or Cr(VI).

Table 4.6 summarizes the results for two such experiments. In the ppb concentration range (Table 4.6a) all of the chromium in the aqueous phase was found to be cationic Cr(III). There was no activity lost to the container walls so that the partition of chromium was a reflection of its oxidation state. In reality this experiment was similar to, but longer than, ones in which the optimum mixing time was determined; ie. the distribution ratio decreased with time because of reduction of the Cr(VI). However, in contrast to the aqueous phase reductions of Cr(VI) at trace levels, the conversion to Cr(III) was slower with the increase in the HCl concentration up to 1M. This can be explained by considering the extraction conditions - less Cr(VI) is partitioned to the aqueous phase from 1M acid and it is probable that most of the reduction occurs in this phase. Since the acid concentration in the organic phase is lower, and the proton is bound to the DPPM as well as the Cr(VI) complex, the acid induced reduction would be expected to be slower in the organic phase. Thus, the comparable rates of reduction are less when the Cr(VI) extract is stored separately in the organic diluent than when in contact with aqueous HCl solutions. At higher Cr(VI) concentrations (Table 4.6b) the loss of activity from the organic to the aqueous phase is much slower. There is also an

Table 4.6

Loss of activity from a labelled solution of Cr(VI) in 0.10 M DPPM/CH_2ClCH_2Cl to aqueous HCl solutions when subjected to continuous mixing of the two phases.

a). Distribution of activity for approximately 20 ppb chromium. Equal volumes of the aqueous and organic phases were mixed and the aqueous phase was monitored at various times.

Aqueous solution	% activity in aqueous phase (± 2%)			
	1.2 h	8 h	22 h	56 h
0.1 M HCl	4	33	52	81
0.5 M HCl	4	20	30	60
1.0 M HCl	3	14	26	52

b). Distribution of activity for 1 x 10^{-3} M Cr(VI), initially in the organic phase, when mixed with two times the volume of aqueous phase. The aqueous phase was monitored at various times.

Aqueous solution	% activity in aqueous phase (± 1%)			
	1.5 h	6 h	21 h	193 h
0.12 M HCl	6	8	10	25
0.12 M HCl + 0.5 M LiCl	4	5	7	19
0.6 M HCl + 0.5 M LiCl	2	4	4	16
1.2 M HCl	<1	3	4	14
1.2 M HCl + 0.5 M LiCl	<1	2	2	12

apparent salt effect, an indication that at a fixed acid concentration the more Cl^- available the more stable the extracted species.

It has been shown that there was no change in the extractant when the organic extracts were stored alone or in contact with acid. Now there was clear evidence that loss of activity from the organic phase was due to an eventual reduction of Cr(VI) when in contact with the acidic solutions. Thus, it seems probable that when stored as an organic extract alone the loss of activity to container walls is because a Cr(III) reduction product is formed which is expelled from the organic phase. An investigation of the activity on the walls of such containers was consistent with the previous results for Cr(III) adsorption on surfaces from aqueous phase systems.

To increase the enrichment factor it should, in theory, be possible to simply increase the extraction ratio. However, there are limitations imposed by the solubility of the organic diluent in the aqueous phase. When using CH_2ClCH_2Cl, which has the lowest solubility in water of any of the effective diluents (0.81 g/100 mL), with extraction ratios of up to 25:1 the separations were satisfactory. At an extraction ratio of 50:1 difficulties arose when 0.10M DPRM/CH_2ClCH_2Cl was mixed with solutions prepared with deionized or tap water. Phase separation required centrifugation and the apparent distribution ratios were only 68 ± 2 and 69 ± 2 respectively. In a re-extraction, with the aqueous phase now saturated by organic phase, the distribution ratio increased significantly. While it was encouraging to see that the extraction from deionized water and tap water were essentially identical when the $^{51}Cr^{3+}$ label was introduced

then oxidized by 1×10^{-3} M Ce(IV), it was clear that little was gained, from an analytical perspective, by increasing the extraction ratio above 25:1.

As long as it remains as Cr(VI), the chromium seems to form a particularly strong attachment to the protonated extractant. However, it does undergo anion exchange on strong anion-exchange resins when the organic phase is passed through an appropriately prepared column. It is also adsorbed quantitatively from the organic phase by alumina, by either column or batch processes. Although it is adsorbed on silica gel it is readily displaced in the presence of any moisture. After displacement by water it is in a cationic form, probably because silica gel is an acidic reagent under such circumstances and promotes a reduction. Nevertheless, if there is a desire to separate the extracted Cr(VI) from the bulk of the diluent any of these substances may be used to achieve this objective.

Further evidence that the Cr(VI) is not readily displaced from the $DPPMH^+$ ion was provided when an attempt was made to form the diphenylcarbazide complex with Cr(VI). While this colored complex could be formed easily with Cr(VI) in aqueous solutions, little reaction was possible with the extracted Cr(VI). The reaction, or lack thereof, was followed by observing the color change or by ion-exchange methods. The conversion of the original anionic Cr(VI) to a cationic species by the diphenylcarbazide was evidence for a reaction, since in the new complex all chromium appears as Cr(III), even below a concentration at which the color is apparent. Thus, a spectrophotometric analysis employing this reagent was not possible.

The conditions for a back extraction were explored since an analysis in the aqeuous phase is sometimes preferred to working with volatile organic extracts and long term sample storage could be more reliable. The most effective means of removing the chromium from the organic phase involved the destruction of the active extractant or displacement and reduction of the Cr(VI). By titrating the organic extract with NaOH or KOH the protonation of the DPPM was destroyed and the chromium was no longer stabilized in the organic phase. However, while this removed the chromium it also produced an aqueous solution with excess alkali metal ions, not generally desirable in analysis by technique such as AAS. A more useful approach involved the introduction of $HClO_4$ into a sample of the extracted Cr(VI). The excess ClO_4^- could compete favorably with the trace of Cr(VI) for the pairing sites on the $DPPMH^+$ and displace a substantial portion of the Cr(VI) to the aqueous phase where it was reduced by the acidic H_2O_2 solution. Since the Cr(III) produced was no longer extracted into the organic phase the ClO_4^- quite quickly displaced the diminishing amount of Cr(VI). Certainly the back extraction was quantitative within 30 minutes when using a 0.1% H_2O_2 solution and 1×10^{-3}M $HClO_4$. Further, in the acidic solution there was no loss of chromium to the walls of the container. Alternative approaches; involving just water, other acids and/or reducing agents; were possible but were not as rapid or quantitative and often produced a solution subject to wall loss or potential interferences in the final analysis.

4.2.3 The extraction model

Despite the statement made by Sekine and Hasegawa[112] about the failure of efforts to understand the equilibria of metal extractions, an attempt to explain the extraction by DPPM was undertaken. Since at trace concentrations the presence of Cr(VI) had no impact on the equilibrium conditions established by the bulk of the DPPM in the various diluents reacting with the HCl originally confined to the aqueous phase, the initial focus was on the acid extraction.

The distribution and reactions resulting from the mixing of DPPM/diluent with solutions of HCl may be represented by the equations:

$$\overline{DPPM} \rightleftharpoons DPPM \qquad K_d = [DPPM]/[\overline{DPPM}] \qquad (4.6)$$

$$DPPMH^+ \rightleftharpoons DPPM + H^+ \qquad K_e = [DPPM][H^+]/[DPPMH^+] \qquad (4.2)$$

$$DPPMHCl \rightleftharpoons DPPMH^+ + Cl^- \qquad K_f = [DPPMH^+][Cl^-]/[DPPMHCl] \qquad (4.7)$$

$$\overline{DPPMHCl} \rightleftharpoons DPPMHCl \qquad K_g = [DPPMHCl]/[\overline{DPPMHCl}] \qquad (4.8)$$

$$\overline{DPPMHCl} \rightleftharpoons \overline{DPPMH^+} + \overline{Cl^-} \qquad K_h = [\overline{DPPMH^+}][\overline{Cl^-}]/DPPMHCl] \qquad (4.9)$$

NOTE: For simplicity the equilibrium constants K_d, K_e, K_f, K_g, K_h have been adoped within this section to designate the constants for the respective reactions.

If one starts with a fixed concentration of DPPM in the organic phase, represented as $[\overline{DPPM}]_o$, and this comes into equilibrium with an aqueous phase whose volume is such that the extraction ratio is $V/\bar{V}$, the conservation of DPPM requires the following relationship at equilibrium:

$$[\overline{DDPM}]_o = [\overline{DPPM}] + (V/\bar{V})[DPPM] + (V/\bar{V})[DPPMH^+] + (V/\bar{V})[DPPMHCl] + [\overline{DPPMHCl}] + [\overline{DPPMH^+}] \qquad (4.10)$$

These equations are written in concentration terms but for the extraction the activity of the various complexes may be more important. However, this introduces a significant complication since the activities cannot be determined directly. As an initial approximation a value of one may be assigned as the activity coefficient for each of the DPPM complexes. Certainly [DPPM] is always very small and this can be justified. For other species in the aqueous phase the concentrations are not always as low. For instance, the sum of $[DPPMH^+]$ and [DPPMHCl] may be as high as 0.025M in CH_2ClCH_2Cl and the concentrations vary considerably as the concentration of HCl changes in the aqueous phase. Yet, most of the extractant resides in the organic phase as either $\overline{DPPM}$ or $\overline{DPPMHCl}$. Since the ion-pair, $\overline{DPPMHCl}$, does not dissociate appreciably there must be little $\overline{DPPMH^+}$. By default, it becomes necessary to assume that the values of $\gamma_{\overline{DPPM}}$ and $\gamma_{\overline{DPPMHCl}}$ are relatively constant and close to one, even though the monitoring of these species confirms a dramatic decrease in $[\overline{DPPM}]$ and an increase in $[\overline{DPPMHCl}]$ as the acidity increases in the aqueous phase in contact with the organic phase. Herein resides a potential source of error in any extraction model.

By substituting the terms represented in equations (4.2) and (4.6 - 4.9) into equation (4.10), and employing activity coefficients only for species other than those involving DPPM, the following relationship is developed:

$$[\overline{DPPM}]_o = [\overline{DPPM}] + K_d \frac{V}{\overline{V}} [\overline{DPPM}] + \frac{K_d}{K_e} \frac{V}{\overline{V}} \gamma_{H^+} [H^+][\overline{DPPM}]$$

$$+ \frac{K_d}{K_e K_f} \frac{V}{\overline{V}} \gamma_{H^+} \gamma_{Cl^-} [H^+][Cl^-][\overline{DPPM}] \qquad (4.11)$$

$$+ \frac{K_d}{K_e K_f K_g} \gamma_{H^+} \gamma_{Cl^-} [H^+][Cl^-][\overline{DPPM}]$$

$$+ \frac{K_d K_h}{K_e K_f K_g} \gamma_{H^+} \frac{\gamma_{Cl^-}}{\overline{\gamma_{Cl^-}}} \frac{[H^+][Cl^-]}{[\overline{Cl^-}]} [\overline{DPPM}]$$

This extraction equation may be simplified to some extent under certain experimental conditions. If $V = \overline{V}$ and the aqueous and organic phases are not appreciably miscible, then the extraction ratio $V/\overline{V} = 1$. Further, the final term in equation (4.11) may be dropped since dissociation of the ion-pair $\overline{DPPMHCl}$ is not evident in any of the diluents used.

Equation (4.11) may be rearranged and simplified:

$$[\overline{DPPM}]_o = [\overline{DPPM}]\{1 + K_d + \frac{K_d}{K_e} \gamma_{H^+} [H^+] + \frac{K_d}{K_e K_f} \gamma_{H^+} \gamma_{Cl^-} [H^+][Cl^-]$$

$$+ \frac{K_d}{K_e K_f K_g} \gamma_{H^+} \gamma_{Cl^-} [H^+][Cl^-]\} \qquad (4.12)$$

It should now be possible to develop the model in terms of the initial concentration of DPPM in the organic diluent, its equilibrium concentration, the activity of the acid in the aqueous phase and the equilibrium constants of the system. If $\gamma_{H^+}[H^+] = \gamma_{Cl^-}[Cl^-]$ equation (4.12) is recognizably of the form

$$y = a + bx + cx^2$$

where $y = [\overline{DPPM}]_o/[\overline{DPPM}]$

$x = (\gamma_{H^+} \gamma_{Cl^-} [H^+][Cl^-])^{\frac{1}{2}}$

$a = 1 + K_d$

$$b = K_d/K_e$$

$$c = (K_d/K_eK_f) + (K_d/K_eK_fK_g)$$

Experimental data may be entered into a curve fitting program and the values of the constants a, b and c obtained. The Apple IIe computer and the Curve Fitter program (P.K. Warme, Interactive Microware, Inc.) plus an optimization program developed at the University of Manitoba were selected to establish the values of the constants that best fit the data.

To illustrate this procedure the extraction of HCl by 0.10M DPPM/CH_2ClCH_2Cl, the best extraction system for Cr(VI), will be examined in some detail. But first, it is necessary to describe the parameters that are used as the "input" for any acid extraction model.

$\overline{[DPPM]}_o$ is fixed once the extractant/diluent solution has been prepared. $\overline{[DPPM]}$ varies as the aqueous acid solution changes. It can be determined indirectly by employing a simple calculation. Since $\overline{[DPPMHCl]}$ can be determined by a direct two phase titration and the amount of extractant in the aqueous phase, essentially $[DPPMH^+]$ and [DPPMHCl], may be found after the $HClO_4$ acidification and extraction:

$$\overline{[DPPM]} = \overline{[DPPM]}_o - \overline{[DPPMHCl]} - ([DPPMH^+] + [DPPMHCl]) \quad (4.14)$$

Since the only reagent introduced in the aqueous phase is HCl, the concentration of this reagent can be determined by an acid-base titration, both before and after equilibrium has been established by mixing with DPPM/diluent. The loss of HCl from the aqueous phase must equal the acid gained by the organic phase - this may be used to confirm the $\overline{[DPPMHCl]}$ as determined by the two phase titration. The equilibrium

acid concentration in the aqueous phase must equal a contribution from unreacted HCl and any protonated DPPM now in the aqueous phase. Since the total acid may be determined by a direct titration and the concentration of protonated DPPM by the $HClO_4$ extraction technique:

$$[HCl]_{equil} = ([HCl]_{orig} - [\overline{DPPMHCl}]) - ([DPPMH^+] + [DPPMHCl])$$
$$= [acid]_{equil} - ([DPPMH^+] + [DPPMHCl]) \qquad (4.15)$$

Since charge balance must be maintained it follows that $[H^+] = [Cl^-] = [HCl]$.

However, it is the activity of the acid that appears in the extraction equation. The activity coefficients, γ_{H^+} and γ_{Cl^-}, must be assigned values. It is reasonable to assume that the mean activity coefficients reported by Harned and Owen[128], and accepted in standard reference sources[186], are quite reliable. In the last three terms of equation (4.11), when γ_{H^+} γ_{Cl^-} $[H^+][Cl^-]$ appear, these values may be used with little controversy. In the third term of equation (4.11) the appearance of γ_{H^+} $[H^+]$ by itself can give rise to some concern. Recently, single ion activities have been reported for HCl solutions by Majima et al.[187] It appears that the activity of the two ions, Cl^- and H^+, are quite different. Nevertheless, the mean values were used in the initial formulation for the extraction model.

The three constants in equation (4.13), a, b, and c, involve the constants K_d, K_e, K_f and K_g. Two of these equilibrium constants, K_e and K_f, pertain to reactions limited to the aqueous phase and, as such, should not depend upon the diluent used in the extraction process. While it has not been possible to evaluate both of these constants by

independent means, it has been possible to determine K_e by the spectrophotometric technique described in Section 4.2.1.

$$K_e = 3.6 \times 10^{-5}$$

The distribution constants, K_d and K_g, will depend upon the diluent used. Qualitatively, K_d and K_g for the different diluents would be expected to be greater when the dielectric constants of the diluent is greater. A reasonable evaluation of these constants may be possible if acceptable values can be assigned to a, b and c in each extraction system.

For the 0.10M DPPM/CH_2ClCH_2Cl system in contact with HCl solutions of varying concentrations the values that are to be entered into the curve fitter program are $y = \overline{[DPPM]}_o/\overline{[DPPM]}$ and x = acid activity. Values such as those in Table 4.2b) may be used, at least up to about 1M in HCl, in this fitting. Real solutions to equation (4.13) must be ones in which the constants (a, b and c) are all positive numbers. Further, a $\simeq$1 since DPPM is so insoluble in water. Under these circumstances a reasonable fit provides the values:

$$a = 1.00 \pm 0.01,\ b = 0.31 \pm 0.02,\ c = 2.6 \pm 0.3$$

With approximate constants for equation (4.13) known it becomes possible to evaluate the equilibrium constants for a number of reactions. From spectral data

$$K_e = 3.6 \times 10^{-5}$$

$$\therefore K_d = b \times K_e = 0.31 \times 3.6 \times 10^{-5} = 1.1 \times 10^{-5}$$

The fact that at a concentration of HCl above about 2M the ratio of the concentrations of protonated DPPM in each phase becomes almost constant permits an estimation of the upper limit for K_g of about 0.35. Thus,

various values may be tried to find the distribution of DPPM complexes in an extraction system. For instance, if

$$K_g = [DPPMHCl]/[\overline{DPPMHCl}] = 0.30$$

$$\text{since } c = \left(\frac{K_d}{K_e K_f}\right) + \left(\frac{K_d}{K_e K_f K_g}\right) = b\left(\frac{1 + K_g}{K_f K_g}\right)$$

$$K_f = b\left(\frac{1 + K_g}{K_g}\right)/c = 0.31\left(\frac{1 + 0.30}{0.30}\right)/2.6 = 0.52$$

Employing these evaluated equilibrium constants a complete table may be prepared for the expected distribution of complexes for any equilibrium concentration of HCl, Table 4.7.

The distribution of DPPM complexes recorded in Table 4.7 is illustrated in Figure 4.12. The experimental values for $[DPPMH^+]$ + [DPPMHCl] and $[\overline{DPPMHCl}]$ are included for comparison - these values are reported in Table 4.2b) and Figure 4.3b) as well. While the calculated curve with the constants chosen does not fit the experimental data exactly, the correspondence is very good over most of the range depicted. It does represent the experimental fact that $[\overline{DPPMHCl}]$ does not exceed $[DPPMH^+]$ + [DPPMHCl] at low HCl concentrations. At higher [HCl] the calculated value for $[\overline{DPPMHCl}]$ somewhat exceeds the experimental value while the sum $[DPPMH^+]$ + [DPPMHCl] is slightly lower than the experimental value. By changing the constants this can be overcome but to the detriment of the fit at lower acidities. The representation adopted seems like a good compromise between extremes and the discrepancies at increasing [HCl] could be accounted for if there is any solubility of the DPPMHCl complex solvated by CH_2ClCH_2Cl in the aqueous acidic layer.

Table 4.7

The distribution of complexes of DPPM after equilibration of 0.10 M DPPM/CH_2ClCH_2Cl with an equal volume of various HCl solutions.

The values are calculated using the constants found by employing the extraction model: a = 1

b = 0.31 and Ke = 3.6×10^{-5} so that Kd = 1.1×10^{-5}

c = 2.6 and Kg = 0.30 so that Kf = 0.52

It is assumed that $a_{H^+} = a_{Cl^-}$.

For comparison purposes the HCl concentration chosen in the calculations corresponds to those represented in the experimental trial illustrated in Table 4.2 b).

[HCl] M	$[\overline{DPPM}]$ M	$[DPPMH^+]$ M	[DPPMHCl] M	$[\overline{DPPMHCl}]$ M
0.118	0.0951	0.0027	0.0005	0.0016
0.352	0.0790	0.0065	0.0033	0.0111
0.577	0.0612	0.0083	0.0070	0.0234
0.802	0.0452	0.0088	0.0106	0.0354
1.142	0.0276	0.0081	0.0148	0.0494
1.314	0.0215	0.0075	0.0164	0.0546
2.172	0.0065	0.0046	0.0205	0.0683
4.804	0.0003	0.0011	0.0227	0.0758

Relationships employed in the calculations:

$$[\overline{DPPM}] = [\overline{DPPM}]_o / [1 + Kd + (\frac{Kd}{Ke} a_{H^+}) + (\frac{Kd}{KeKf} a_{H^+} a_{Cl^-}) + (\frac{Kd}{KeKfKg} a_{H^+} a_{Cl^-})]$$

$$[DPPMH^+] = \frac{Kd}{Ke} [\overline{DPPM}] a_{H^+} = b[\overline{DPPM}] a_{H^+}$$

$$[DPPMHCl] = \frac{Kd}{KeKf} [\overline{DPPM}] a_{H^+} a_{Cl^-} = [DPPMH^+] a_{Cl^-}/Kf$$

$$[\overline{DPPMHCl}] = \frac{Kd}{KeKfKg} [\overline{DPPM}] a_{H^+} a_{Cl^-} = [DPPMHCl]/Kg$$

Figure 4.12

The distribution of DPPM complexes for a system composed of 0.10 M DPPM/CH_2ClCH_2Cl in equilibrium with hydrochloric acid of varying activities. The curves are calculated using the equilibrium constants determined for the equations involved in the extraction model.

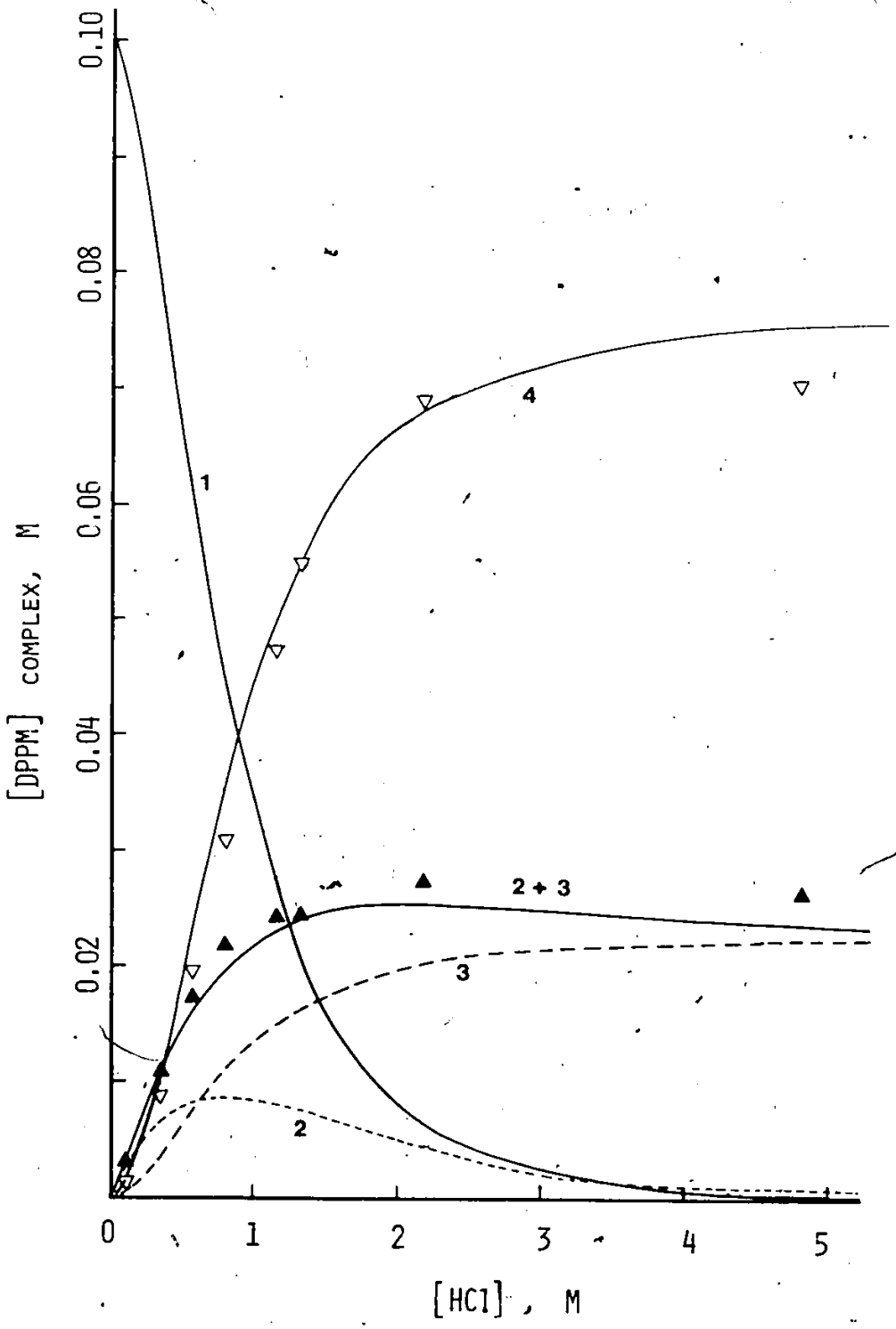
1. $[\overline{DPPM}]$
2. $[DPPMH^+]$
3. $[DPPMHCl]$
4. $[\overline{DPPMHCl}]$

$2 + 3.\ [DPPMH^+] + [DPPMHCl]$

Experimental values for comparison only.

▲ $[DPPMH^+] + [DPPMHCl]$

▽ $[\overline{DPPMHCl}]$


0,10
0,08
0,06
0,04
0,02
[DPPM] COMPLEX, M
1
2
3
2 + 3
4
0
1
2
3
4
5
[HCl], M

Thus, some approximate values for the equilibrium constants of the equations suggested for a model extraction system involving 0.10M DPPM/diluent are available:

In the aqueous phase:

$K_e = 3.6\ (\pm 0.1) \times 10^{-5}$, $K_f = 0.52\ (\pm 0.1)$

In CH_2ClCH_2Cl

$K_d = 1.1\ (\pm 0.1) \times 10^{-5}$, $K_g = 0.30\ (\pm 0.05)$

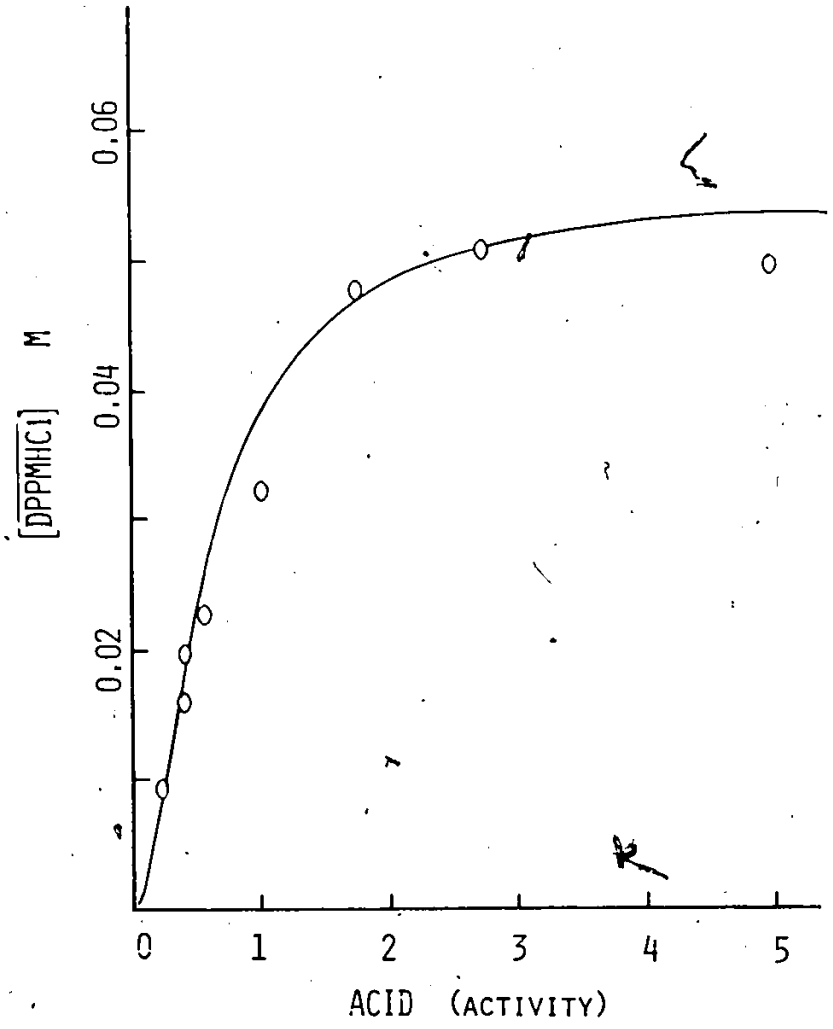
If these values are valid it should be possible to use them to predict the effect of a change in the extraction ratio on the acid extraction by 0.10M DPPM/CH_2ClCH_2Cl. By reintroducing the volume relationships in equation (4.12) the values calculated for $[\overline{DPPMHCl}]$ when $V/\bar{V} = 5/2$ are represented in Figure 4.13. Several experimental points are depicted but comparison of the calculated curve with Figure 4.2, albeit the acid is in different units, is also possible.

The effect of added chloride salt should be predictable, although the activities in mixed systems can be more difficult to deal with than the already complicated acid case and this could make quantitative evaluations very tentative. However, in the presence of LiCl the reaction represented by equation (4.7) would be shifted to the left. The increase in [DPPMHCl] at the expense of $[DPPMH^+]$ would be reflected in an increase in $[\overline{DPPMHCl}]$. Experimentally it was shown that at low acid concentrations in which $[DPPMH^+] + [DPPMHCl] > [\overline{DPPMHCl}]$, the addition of salt caused a shift in the equilibrium concentration of the DPPM complexes, and $[\overline{DPPMHCl}]$ increased with an increase in [LiCl] so that $[\overline{DPPMHCl}] > [DPPMH^+] + [DPPMHCl]$ - see Table 4.3b).

Figure 4. 13

The predicted concentration of $\overline{\text{DPPMHCl}}$ in an extraction system involving 5 mL of an aqueous HCl solution and 2 mL of 0.10 M DPPM/CH_2ClCH_2Cl. The constants and equilibrium conditions for the extraction model are used to determine the variation of [$\overline{\text{DPPMHCl}}$] with changes in the acid activity.

Experimental values for comparison only. O


[DPPMHCl] M
0.06
0.04
0.02
0
1
2
3
4
5
ACID (ACTIVITY)

Application of the acid extraction model should be as valid for CH_2Cl_2 and $CHCl_3$ as it is for CH_2ClCH_2Cl as a diluent. In actual fact, the only major differences should be in the values of the distribution constants represented as K_d and K_g. The aqueous phase reactions should be affected little by variations in the diluent.

By minimizing the variance when fitting the extraction data for 0.10M DPPM/CH_2Cl_2 the values for the constants in equation (4.13) were found to be:

$$a = 1.00 \pm 0.01,\ b = 0.29 \pm 0.02,\ c = 4.5 \pm 0.5.$$

With these values it is apparent the K_d in CH_2Cl_2 is marginally smaller than K_d in CH_2ClCH_2Cl but K_g is much smaller. For example, if one assumes K_f is independent of diluent and has a value of 0.52, then:

$$K_g = \frac{b}{(cK_f - b)} = \frac{0.29}{(4.5)(0.52)-(0.29)} = 0.14 \text{ in } CH_2Cl_2.$$

This value is somewhat higher than the maximum limit of 0.12 estimated from experimental results but within the error limitations of the analysis. Perhaps the value for K_f assigned by the fitting procedure in the 0.1M DPPM/CH_2ClCH_2Cl system is somewhat low.

To illustrate the use of the model both the effect of variations in [HCl] with a fixed 0.10M DPPM/CH_2Cl_2 system (Table 4.8a)) and the effect of changing the $[\overline{DPPM}]_o$ at a fixed initial [HCl] of 1.2M (Table 4.8b)) are displayed. Again, agreement with the experimental results is within an acceptable range. Further, as indicated in Table 4.8b), it seems that the model can be used at diminished DPPM concentrations and it may be possible to explore the distribution of complexes at the much lower concentration accessible by spectrophotometric methods.

The extraction of HCl by 0.1M DPPM/$CHCl_3$ was not examined in as

Table 4.8

The distribution of complexes of DPPM from solutions made up in CH_2Cl_2 and equilibrated with HCl. Theoretical calculations are completed as for Table 4.7 with the constants chosen as follows:

$$b = 0.29, \quad c = 4.5$$

$$Kd = 1.0 \times 10^{-5}, \quad Ke = 3.6 \times 10^{-5}, \quad Kf = 0.62, \quad Kg = 0.10$$

a). The effect of variations in [HCl] with 0.10 M DPPM/CH_2Cl_2

[HCl] M	$[\overline{DPPM}]$ M	$[DPPMH^+]$ M	[DPPMHCl] M	$[\overline{DPPMHCl}]$ M
0.179	0.0879	0.0035	0.0008	0.0078
0.749	0.0343	0.0058	0.0054	0.0544
0.866	0.0277	0.0056	0.0061	0.0607
0.714	0.0068	0.0032	0.0082	0.0819
4.612	0.0002	0.0006	0.0090	0.0902

For experimental values compare Table 4.2 a) and Figure 4.3 a).

b). The effect of changing $[\overline{DPPM}]_o$ at a constant initial [HCl] of 1.2 M

$[\overline{DPPM}]_o$ M	$[\overline{DPPM}]$ M	$[DPPMH^+]$ M	[DPPMHCl] M	$[\overline{DPPMHCl}]$ M
0.1014	0.0175	0.0048	0.0072	0.0719
0.0676	0.0111	0.0031	0.0049	0.0485
0.0338	0.0054	0.0015	0.0024	0.0244
0.0101	0.0016	0.0005	0.0007	0.0074
0.0054	0.0005	0.0002	0.0002	0.0025

For comparison to experimental values see Figure 4.4 a).

much detail as with the other diluents but the behavior resembles that in CH_2Cl_2 more than that in CH_2ClCH_2Cl. However, K_g seems to be a bit smaller than the value in CH_2Cl_2.

The comparison of the extractions of HCl using the effective diluents permits some generalizations. The model accounts for the fact that HCl is extracted into the organic phase of a 0.10M DPPM/diluent system best in the order: $CHCl_3 > CH_2Cl_2 > CH_2ClCH_2Cl$.

The approach taken by Smulek and Siekierski[140] in classifying diluent effects on an operational basis seems to be quite applicable in this case. The interaction of diluent with extractant must change little with the three organic solvents used, but the interaction with the extracted complex must change to a considerable extent; in the terms utilized herein, K_d decreases slightly with a decrease in diluent polarity but K_g decreases markedly.

Also, similar to the situation noted by Kertes and Grauer[141], chloroform seems to stabilize the DPPMHCl salt substantially through some solvation process, probably involving hydrogen bonding. In the other diluents the salt is present to a similar extent and probably stabilized in a like manner, but the distribution varies somewhat. In particular, with CH_2ClCH_2Cl the proportion of salt in the aqueous phase is much greater. While the free-energy change in going from the aqueous phase to the organic phase should be less with CH_2ClCH_2Cl, because it has a higher dielectric constant, that does not lead to greater extraction of HCl. In fact, as the dielectric constant of the diluent becomes closer to that of the aqueous phase there is a more equitable distribution of the DPPMHCl. With a greater availability of DPPMHCl in

the aqueous phase one might suggest that other anions also present in the aqueous phase could more effectively compete with the Cl^- for the pairing sites on the $DPPMH^+$. However, to be preferentially extracted the alternative anions would probably have to be large[144] and/or have a low free-energy of anion hydration in the aqueous phase[145] and form a tightly bound ion-pair with $DPPMH^+$.

It may be possible to explain the extraction of anionic Cr(VI) utilizing the model so far developed. But first, the equilibrium concentration of each Cr(VI) species would have to be considered. To some extent this is predictable by writing the equilibrium equations (2.2) to (2.8) and (2.15). Unfortunately, the equilibrium constant for equation (2.15) is not available and many of the other constants are not agreed upon. Nevertheless, if trace levels of Cr(VI) are used, the introduction of a fixed concentrations of Cr(VI), say $[Cr(VI)]_o$, into an aqueous solution containing HCl must give rise to the following situation:

$$[Cr(VI)]_o = [CrO_4^{2-}] + [HCrO_4^-] + [H_2CrO_4] + [CrO_3Cl^-] + [HCrO_3Cl] \quad (4.16)$$

However, since $[CrO_4^{2-}]$ will be negligible the actual solution could contain the remaining species in a distribution such as that represented in Figure 2.3.

The protonation of DPPM by HCl leads to the formation of $DPPMH^+$ and/or DPPMHCl. A competing anion could form an ion-pair directly by reacting with $DPPMH^+$ or by displacing the Cl^- from the DPPMHCl. In either case, the net effect may be represented as a reaction of $DPPMH^+$ with the anion in question. This new ion-pair may then be extracted

into the organic phase in an extraction system. Thus, in the presence of Cr(VI) the following reactions should be considered:

$$DPPMHCrO_3Cl \rightleftharpoons DPPMH^+ + CrO_3Cl^- \qquad K_p = \frac{[DPPMH^+][CrO_3Cl^-]}{[DPPMHCrO_3Cl]} \qquad (4.17)$$

$$\overline{DPPMHCrO_3Cl} \rightleftharpoons DPPMHCrO_3Cl \qquad K_q = \frac{[DPPMHCrO_3Cl]}{[\overline{DPPMHCrO_3Cl}]} \qquad (4.18)$$

$$DPPMHHCrO_4 \rightleftharpoons DPPMH^+ + HCrO_4^- \qquad K_r = \frac{[DPPMH^+][HCrO_4^-]}{[DPPMHHCrO_4]} \qquad (4.19)$$

$$[\overline{DPPMHHCrO_4}] \rightleftharpoons [DPPMHHCrO_4] \qquad K_s = \frac{[DPPMHHCrO_4]}{[\overline{DPPMHHCrO_4}]} \qquad (4.20)$$

Of major significance are the following equilibrium constants as well:

$$K_{2.2} = \frac{[H^+][HCrO_4^-]}{[H_2CrO_4]} \approx 6.3$$

$$K_{2.7} = \frac{[CrO_3Cl^-]}{[HCrO_4^-][HCl]} \approx 10.7$$

$$K_{2.15} = \frac{[HCrO_3Cl]}{[CrO_3Cl^-][H^+]} \approx 5$$

If the extraction ratio $V/\overline{V} = 1$ then:

$$[Cr(VI)]_o = [H_2CrO_4] + [HCrO_4^-] + [CrO_3Cl^-] + [HCrO_3Cl] \qquad (4.21)$$
$$+ [DPPMHCrO_3Cl] + [DPPMHHCrO_4] + [\overline{DPPMHCrO_3Cl}] + [\overline{DPPMHHCrO_4}]$$

Rewriting this equation and inserting the appropriate activities for the HCl but not the Cr(VI), since it is at a trace concentration and the activities and concentrations should be equal, yields the following result:

$$[Cr(VI)]_o = [H_2CrO_4]\left(1 + \frac{K_{2.2}}{a_{H^+}} + K_{2.7}K_{2.2}a_{Cl^-} + K_{2.15}K_{2.7}K_{2.2}a_{H^+}a_{Cl^-} + [DPPMH^+]\left[\frac{K_{2.7}K_{2.2}a_{Cl^-}}{K_p} + \frac{K_{2.7}K_{2.2}a_{Cl^-}}{K_pK_q} + \frac{K_{2.2}}{a_{H^+}K_r} + \frac{K_{2.2}}{a_{H^+}K_rK_s}\right]\right) \qquad (4.22)$$

It can be seen that given enough information it should be possible to work out the Cr(VI) concentration in each of the potential species present in an extraction system.

Thus, the distribution ratio

$$D = \frac{[\overline{Cr(VI)}]}{[Cr(VI)]} = \frac{[\overline{DPPMHCrO_3Cl}] + [\overline{DPPMHHCrO_4}]}{\text{all } [Cr(VI)]}$$

$$\text{But } [\overline{DPPMHCrO_3Cl}] = \frac{[DPPMH^+][CrO_3Cl^-]}{K_pK_q} \qquad (4.23)$$

$$\text{and } [\overline{DPPMHHCrO_4}] = \frac{[DPPMH^+][HCrO_4^-]}{K_rK_s}$$

The $[\overline{Cr(VI)}]$ extracted will depend upon the concentration of $DPPMH^+$ in the system and the proportions of each of the anionic Cr(VI) species. If the extraction model is correct it is apparent that since $[DPPMH^+]$ is at a maximum near 1M in HCl this could influence the distribution ratio. Further, if CrO_3Cl^- is the main Cr(VI) species extracted this would lead to a maximization of the distribution ratio near 1M in HCl.

It is now possible to rewrite equation (4.23) incorporating the information from equation (4.22).

$$D = \frac{[DPPMH^+]\left(\frac{K_{2.7}K_{2.2}a_{Cl^-}}{K_pK_q} + \frac{K_{2.2}}{a_{H^+}K_rK_s}\right)}{1+\frac{K_{2.2}}{a_{H^+}}+K_{2.7}K_{2.2}a_{Cl^-}+K_{2.15}K_{2.7}K_{2.2}a_{H^+}a_{Cl^-}+[DPPMH^+]\left(\frac{K_{2.7}K_{2.2}a_{Cl^-}}{K_p} + \frac{K_{2.2}}{a_{H^+}K_r}\right)} \quad (4.24)$$

Notice that D is independent of the $[Cr(VI)]_o$. It depends only upon the activity of the acid and upon $[\overline{DPPM}]_o$ - since $[DPPMH^+]$ depends upon the acidity and $[\overline{DPPM}]_o$, and the Cr(VI) proportions depend upon the acidity.

It remains to determine acceptable values for K_p, K_q, K_r and K_s. One approach is to solve for the 4 unknowns using a minimum of 4 equations and the distribution ratios, D, found experimentally. However, the mathematical solution need not make the most sense chemically and will depend markedly on the validity of the constants selected in the equations.

Using such an approach the following values were assigned to the constants for a 0.1M DPPM/CH_2Cl_2 extractant:
$K_p = 2.5 \times 10^{-3}$, $K_q = 1.0 \times 10^{-3}$, $K_r = 2.5 \times 10^{-4}$, $K_s = 2.5 \times 10^{-2}$.
By utilizing these values in equation (4.24) the distribution ratio was calculated for several concentrations of HCl.

$$D = \frac{[DPPMH^+]\left(\frac{67.4\,a_{Cl^-}}{K_pK_q} + \frac{6.3}{K_rK_sa_{H^+}}\right)}{1+6.3/a_{H^+}+67.4\,a_{Cl^-}+337\,a_{H^+}a_{Cl^-}+[DPPMH^+]\left(\frac{67.4a_{Cl^-}}{K_p} + \frac{6.3}{K_ra_{H^+}}\right)}$$

[HCl], M	0.2	0.6	0.8	1.0	1.2	2.0
D,calc	58	168	206	212	193	85

These calculated values may be compared to the representation in Figure 4.8. While the maximum experimental value for D is somewhat higher than the maximum calculated value using these constants the trend is almost perfectly matched. D increases with the initial increase in [HCl] but decreases as [HCl] exceeds 1M.

Since reaction (4.17) and reaction (4.19) should be independent of the diluent one would expect that in CH_2ClCH_2Cl the same values for K_p and K_r may be acceptable. However, K_q and K_s may be smaller in CH_2ClCH_2Cl than in CH_2Cl_2. Using the values $K_p = 2.5 \times 10^{-3}$, $K_q = 5 \times 10^{-4}$, $K_r = 2.5 \times 10^{-4}$ and $K_s = 3 \times 10^{-3}$ the calculations for the 0.1M DPPM/$CH_2ClCH_2ClCH_2Cl$ system were completed with the results:

[HCl], M	0.2	0.6	0.8	1.0	1.2	2.0
D, calc	348	530	603	626	598	313

By comparing these values to those illustrated in Figure 4.9 it is apparent that again the trend is reasonable. Discrepancies due to the fixing of the assigned constants or erroneous literature values need not discredit the extraction model.

In fact, the model may be used to explain a number of the experimental observations quite well. The effect of changing the HCl concentration or the $\overline{DPPM}$ concentration can be accounted for. It also helps explain why changing the acid or adding salts can influence the distribution ratio of Cr(VI). Since CrO_3Cl^- is extracted better than $HCrO_4^-$ any change in the effective concentration of CrO_3Cl^- will change the distribution ratio. Further, the addition of substances that reduce the availability of $DPPMH^+$ will diminish the extraction of Cr(VI).

4.2.4 Spectral analysis

For the most part, descriptions of analyses by spectrophotometric methods have been held in abeyance. However, such techniques provide both interesting results which confirm some of the data obtained by the titration and radiotracer procedures and additional information which supports the extraction model.

UV/visible spectra

The absorption of DPPM at the working concentration of 0.1M DPPM/diluent is too intense to be monitored. However, the examination of 1×10^{-4}M DPPM proved to be possible and supportive of the results at higher concentrations as well as useful in establishing the dissociation constant for the protonated species in the aqueous phase.

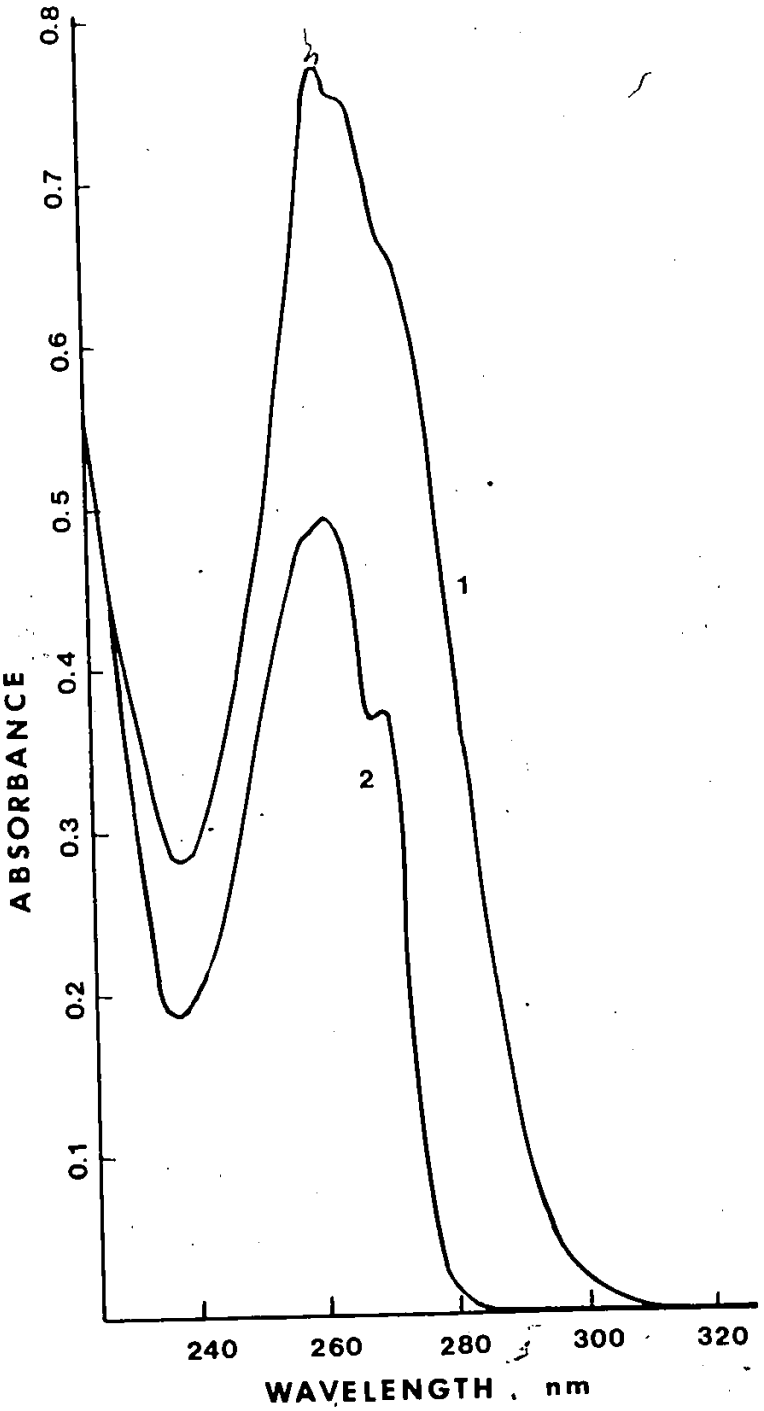
A 1.0×10^{-4}M solution of DPPM dissolved in 0.01M aqueous hydrochloric acid had an absorption maximum at 263 nm as illustrated in Figure 4.14. In 0.03M potassium hydroxide the same nominal concentration had a much different spectrum and a lower absorbance as shown in Figure 4.14. As mentioned, in the experiment designed to establish the dissociation constant for $DPPMH^+$ in aqueous solutions, solutions buffered to pH values intermediate between these extremes had different absorbances and modified spectral characteristics. The spectrum of DPPM as a saturated solution in deionized water at a measured pH 6.3 was similar to that in the dilute KOH solution. Since the optical density of this sample at 263 nm was 0.456 cm^{-1} the limit of solubility of DPPM in water appears to be about 1×10^{-4}M.

The spectra of DPPM in organic diluents differ somewhat from

Figure 4.14

The spectrum of 1 x 10^{-4}M DPPM

1. in a 0.01 M aqueous hydrochloric acid solution
2. in a 0.03 M aqueous sodium hydroxide solution


ABSORBANCE
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
1
2
240
260
280
300
320
WAVELENGTH . nm

those in water. In Figure 4.15 the spectrum of 1.0×10^{-4}M DPPM/CH_2ClCH_2Cl is shown. When compared to that in water the absorption maximum is somewhat blunted.

To totally protonate DPPM in the organic phase is not simple, for when mixed with an aqueous acidic solution there is generally a substantial loss of DPPM to the aqueous phase. However, according to the titration data, when placed in contact with a 1M $HClO_4$ solution the DPPM should be protonated in the organic phase. The 1.0×10^{-4}M DPPM/CH_2ClCH_2Cl solution was mixed with an equal volume of 1.0M $HClO_4$ and the spectra were taken of both the aqueous and organic phases. Any absorbance in the aqueous phase could not be distinguished from base line noise, but was at a maximum 0.002 at 263 nm. The organic phase spectrum is shown in Figure 4.15. While broader than the corresponding spectrum of DPPM in aqueous HCl solution, it too has a slightly lower maximum absorbance.

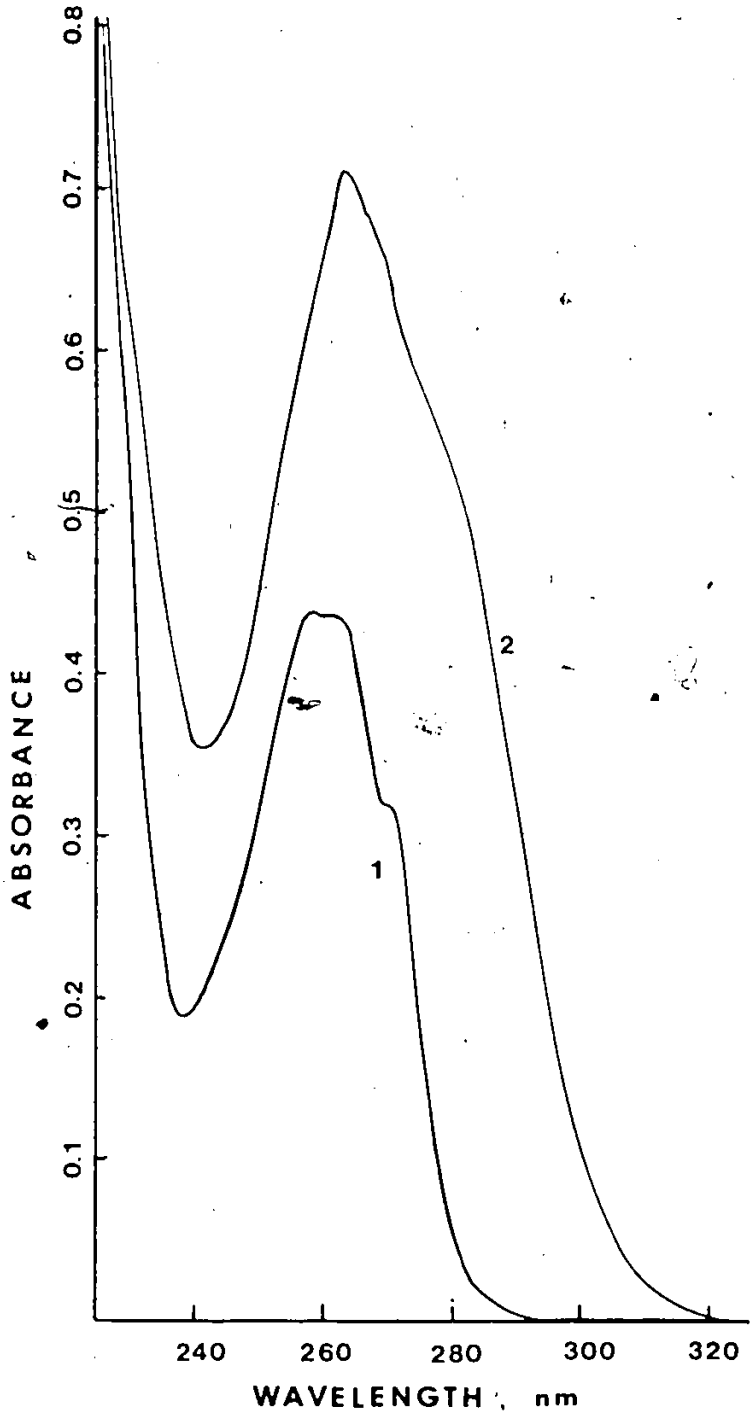
These experiments demonstrated that for some reason, possibly relating to differences in solvation, the absorbance of DPPM and its complexes are not quite as strong in the organic diluents as in water. However, of considerable gratification was the confirmation that in the presence of $HClO_4$ the protonated DPPM favors the organic phase. With 1M $HClO_4$ at a concentration of from 1×10^{-4} to 0.1M DPPM/diluent the complex designated as $DPPMHClO_4$ is completely extracted.

Titration data could not establish the presence of molecular DPPM in any aqueous phase after equilibration of 0.10M DPPM/diluent with an aqeuous acidic solution. Could spectrophotometric techniques provide this information? To try to estimate the distribution constant for the

Figure 4.15

The spectrum of 1×10^{-4}M DPPM

1. in CH_2ClCH_2Cl
2. in CH_2ClCH_2Cl after equilibrating the solution with 1 M $HClO_4$.


ABSORBANCE
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
1
2
240
260
280
300
320
WAVELENGTH, nm

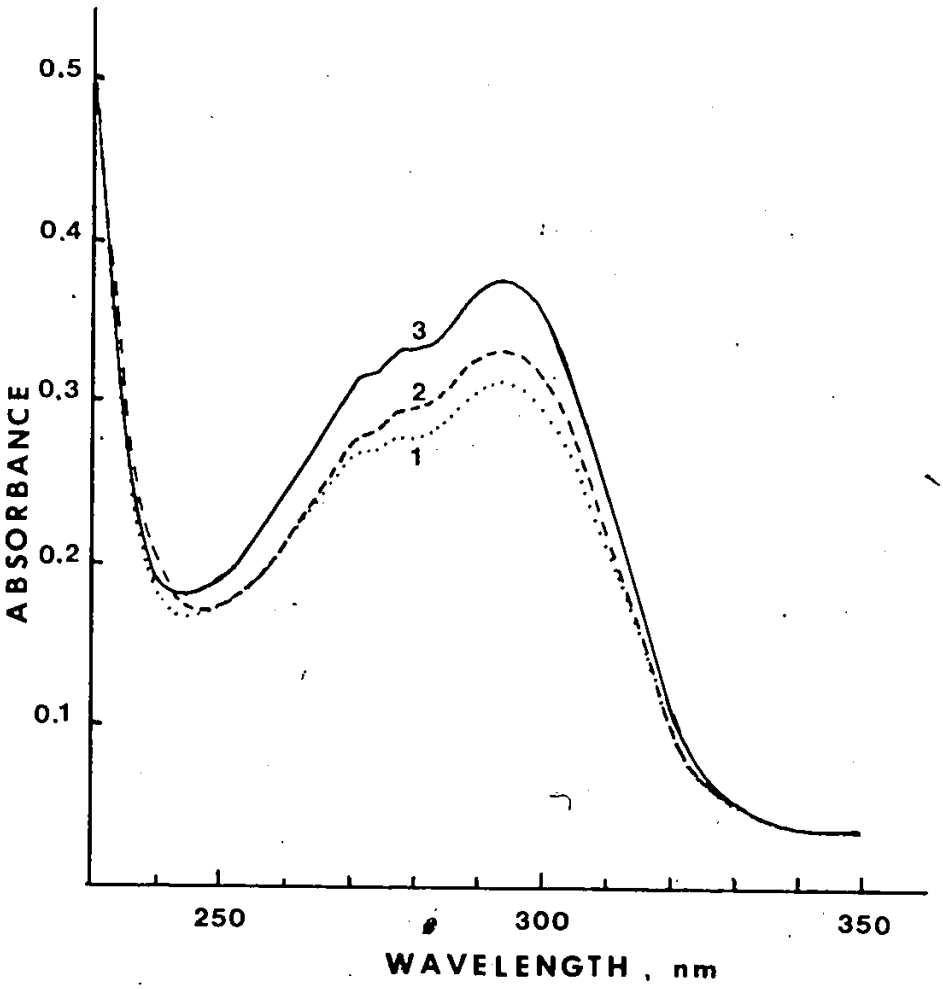
partition represented by equation (4.6) a sample of each 0.10M DPPM/diluent solution was mixed with water, the phases were separated and the spectra examined. Figure 4.16 depicts these spectra. Interpretation is made difficult because there is a shift from the maxima expected in water or diluent. However, with a decrease in the concentration of DPPM used there was a corresponding decrease in the absorbance, so that signals are due to DPPM complexes. It is suspected that there is some solvation of the DPPM by the diluent and, when transferred to the aqueous phase, this changes the spectral response from that expected for molecular or protonated DPPM in one solvent alone. Nevertheless, these spectra do provide insight into the distribution of DPPM. An increase in the dielectric constant of the diluent, as it becomes closer to that of the water with which it is in contact, permits more removal of DPPM to the aqueous phase. Thus, the DPPM concentration available for protonation in the aqueous phase increases from $CHCl_3$ to CH_2Cl_2 to CH_2ClCH_2Cl. But even in CH_2ClCH_2Cl the concentration of DPPM in the aqueous phase is less than 1×10^{-4}M, and much of that need not be aquated but may be associated with diluent which is dissolved to its solubility limit.

The partition of 1×10^{-4}M DPPM between CH_2ClCH_2Cl and various aqueous solutions was explored spectrophotometrically. From the previous discussion regarding the species determined by the titration techniques and the evidence for the very limited dissolution of DPPM in an aqeuous phase, it is apparent that the absorption in the aqeuous phase would be due to $[DPPMH^+]$ and/or [DPPMHCl]. In the organic phase absorption for both $\overline{[DPPM]}$ and $\overline{[DPPMHCl]}$ would be probable. By

Figure 4.16

The spectrum in neutral water after having mixed and separated an equal volume of 0.10 M DPPM/diluent with the water:

1. $CHCl_3$ used as diluent
2. CH_2Cl_2 used as diluent
3. CH_2ClCH_2Cl used as diluent


0.5
0.4
0.3
0.2
0.1
ABSORBANCE
3
2
1
250
300
350
WAVELENGTH , nm

equilibrating the solutions and measuring the absorbance of the separated phases at λ = 263 nm it becomes possible to estimate the concentration of the complexes in each phase. In Table 4.9 the data and results are summarized. The final results are depicted in Figure 4.17 as well.

The results are quite similar to the expectations from the titration data in the much higher 0.10M DPPM/CH_2ClCH_2Cl situation. Discrepancies are more likely due to shifts in the absorption maximum or extinction coefficients selected than to any difference in the equilibrium at the two concentrations. For example, $\varepsilon_{\overline{DPPMHCl}}$ is not directly measurable and the value has been assigned as that found for $\varepsilon_{DPPMH^+ + DPPMHCl}$. In fact, its value could be closer to that of $\varepsilon_{\overline{DPPMHClO}} = 7.25 \times 10^3\ M^{-1}\ cm^{-1}$. If this lower value was used, as the HCl concentration increased the calculated values for $[\overline{DPPM}]$ would decrease and for [DPPMHCl] would increase more rapidly. Nevertheless, the pattern would be the same and almost identical to that found by the titration method at the higher concentration of DPPM, as illustrated in Figure 4.3b).

Before turning to the spectrophotometric examination of the extraction of Cr(VI) some general comments are in order. Although the absorption by the 0.1M DPPM/diluent does not permit examination of chromium absorption bands below 300 nm there are still the major bands near 370 nm and 455 nm to work with. These electronic bands are attributed to the $^1A_1(t_1^6) \rightarrow {}^1T_1(t_1^5e)$ and $^1A_1(t_1^6) \rightarrow {}^1T_2(t_1^5e)$ charge transfer transition respectively.[188] In alkali media, where Cr(VI) exists almost exclusively as CrO_4^{2-} ions, the strong absorptions near

TABLE 4.9

Determination of the distribution of DPPM complexes by spectrophotometric methods. The absorbance of the separated phases was measured in a 1 cm cell at λ = 263 nm after mixing equal volumes of 1.0×10^{-4} M DPPM/CH_2ClCH_2Cl with solutions of hydrochloric acid of the concentrations specified. The concentration of each DPPM species considered important was calculated from this absorbance data by the procedure indicated below.

[HCl] (orig. aq.)	Abs (aq)	$[DPPMH^+]$ + [DPPMHCl] ($M \times 10^4$)	$\overline{Abs}$ (org)	$[\overline{DPPM}]$ ($M \times 10^4$)	$[\overline{DPPMHCl}]$ ($M \times 10^4$)
0.01	0.018	0.024	0.447	0.968	0.010
0.11	0.080	0.106	0.442	0.887	0.052
0.23	0.080	0.106	0.415	0.871	0.026
0.39	0.105	0.139	0.406	0.781	0.068
0.81	0.178	0.236	0.373	0.665	0.094
1.00	0.202	0.268	0.360	0.645	0.089
1.21	0.212	0.281	0.422	0.389	0.325
1.61	0.232	0.307	0.474	0.176	0.522
1.94	-	-	0.481	0.123	0.575
3.02	0.226	0.299	0.522	0.024	0.677

The concentration of each species was calculated by manipulation of the general formula

$$Abs = \epsilon CL$$

DPPM protonated in the aqueous phase was calculated as:

$$[DPPMH^+ + DPPMHCl] = Abs/\epsilon L$$

when $\epsilon_{DPPM^+ + DPPMHCl} = 7.55 \times 10^3\ M^{-1}\ cm^{-1}$

From the graph (Figure 4.11), the best values were used in the calculation of the concentrations of the DPPM complexes in the organic phase.

For convenience $[\overline{DPPM}] = x$

$$[\overline{DPPMHCl}] = [\overline{DPPM}]_o - [\overline{DPPM}] - [DPPMH^+ + DPPMHCl]$$

$$= (1.0 \times 10^{-4}) - (x) - [DPPMH^+ + DPPMHCl]$$

Using $\epsilon_{\overline{DPPM}} = 4.54 \times 10^3\ M^{-1}\ cm^{-1}$

$\epsilon_{\overline{DPPMHCl}} = 7.55 \times 10^3\ M^{-1}\ cm^{-1}$

it follows that

$$Abs = [\overline{DPPM}] \times \epsilon_{\overline{DPPM}} \times L + [\overline{DPPMHCl}] \times \epsilon_{\overline{DPPMHCl}} \times L$$

$$= 4.54 \times 10^3\ (x) + 7.55 \times 10^3\ (1.0 \times 10^{-4} - x - [DPPMH^+ + DPPMHCl]$$

The values of all DPPM species considered important are illustrated in Figure 4.17.

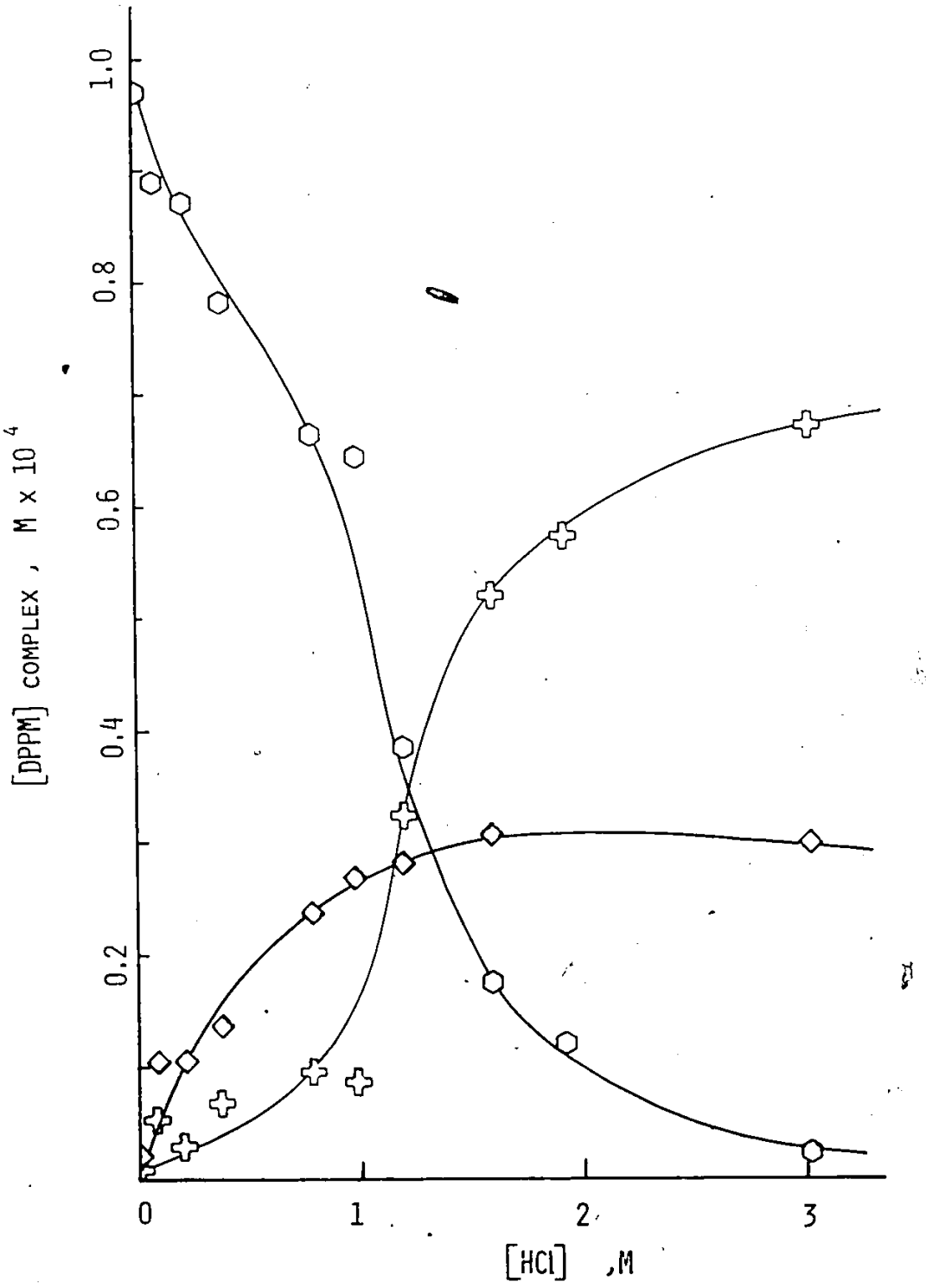
Figure 4.17

The graphical representation of the distribution of DPPM complexes for a system of 1 x 10^{-4}M DPPM/CH_2ClCH_2Cl mixed with an equal volume of aqueous hydrochloric acid of varying concentrations. The absorbance in each phase was measured at λ = 263 nm and the concentration for the different DPPM complexes calculated.


$[\overline{DPPM}]$


$[\overline{DPPMHCl}]$


$[DPPMH^+ + DPPMHCl]$


[DPPM] COMPLEX , M x 10 4
1.0
0.8
0.6
0.4
0.2
0
1
2
3
[HCl] ,M

375 nm ($\varepsilon \simeq 5000$) have been used in the analysis of Cr(VI) in the 1 - 10 ppm region.[179] In acidic solutions an analytical evaluation using this absorption band is less common but still possible, with claims that Cr(VI) between 2 and 40 ppm can be estimated accurately at 350 nm ($\varepsilon \simeq 1500$).[179,180] The fact that Cr(VI) in perchloric acid of pH 3 has been adopted as a standard in spectrophotometry because of the good long-term stability of the solutions having nominal absorbances of 0.2 to 1.2 at 350 nm[189] means that the spectral characteristics have been well studied and generally agreed upon.

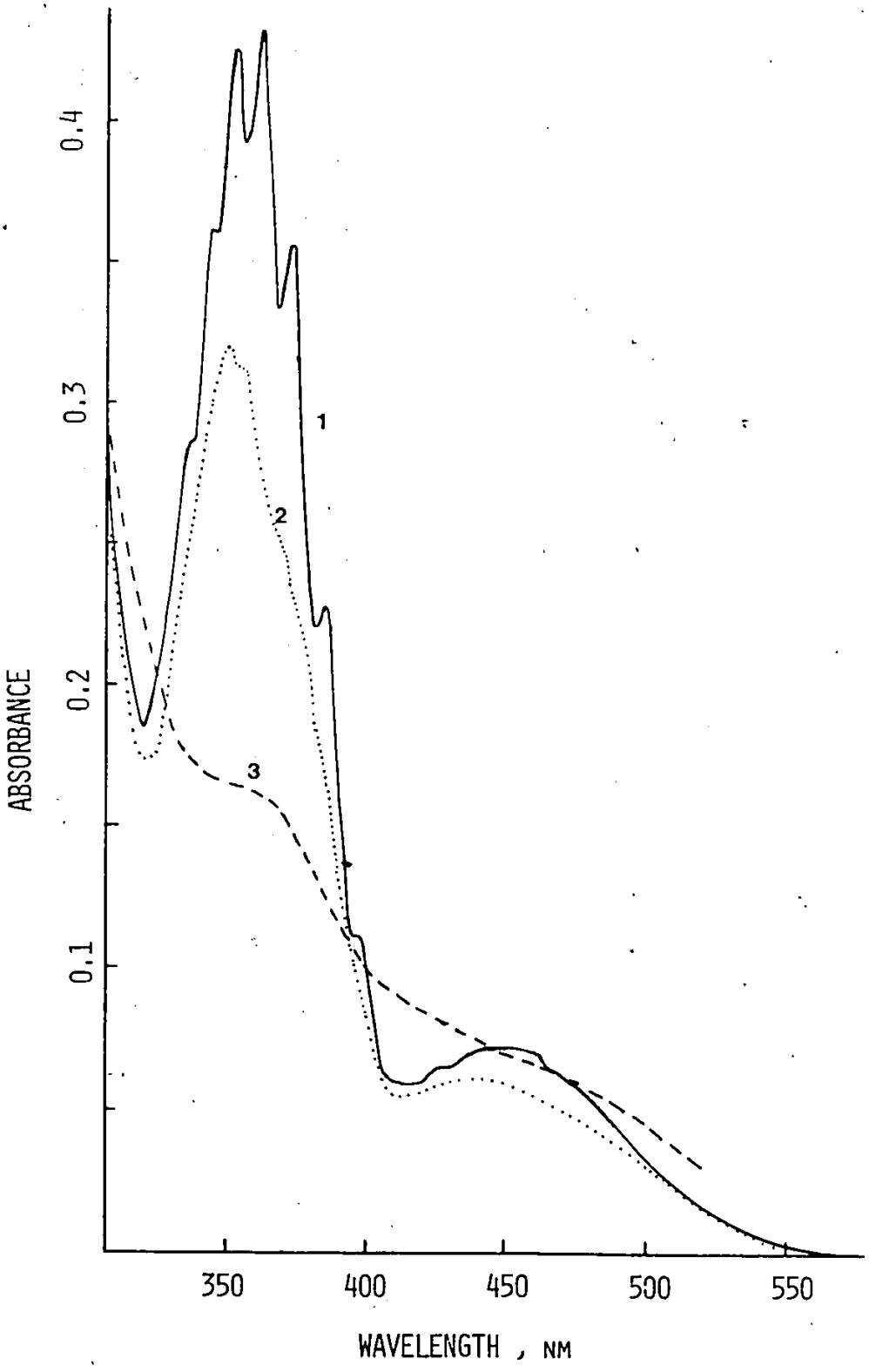
However, the direct spectrophotometric analysis of Cr(VI) is subject to considerable interference problems.[179,180] Adam and Pribil[38] tried to overcome these problems by selective extraction of Cr(VI) into TnOA/diluent and did have some success in using the absorbance near 450 nm. Since the absorbance near 350 nm is stronger it seemed that the possibility of using this spectral region in Cr(VI) analysis, once separated into an extract, should be explored.

Radiotracer studies have shown that the Cr(VI) is almost quantitatively extracted into 0.10M DPPM/CH_2ClCH_2Cl from 1M HCl solutions, extracted to a considerably extent from H_2SO_4 solutions of a similar concentration, but extracted poorly from solutions of HNO_3. As long as the Cr(VI) is not reduced there appears to be no difference in the extractability at different concentrations so that a spectral analysis should be possible in the 2 to 40 ppm concentration region in which the absorption is of an appropriate magnitude. The spectra for the extraction of 16.7 ppm Cr(VI), as $K_2Cr_2O_7$, from HCl, H_2SO_4 and HNO_3 solutions are illustrated in Figure 4.18. Clearly, the extractability

Figure 4.18

The organic phase spectra when an equal volume of 0.10 M DPPM/CH_2ClCH_2Cl is mixed with 16.7 ppm $Cr_2O_7^{2-}$ in an aqueous acidic solution of:

1. 1.0 M HCl
2. 0.6 M H_2SO_4
3. 0.5 M HNO_3


ABSORBANCE
0,4
0,3
0,2
0,1
1
2
3
350
400
450
500
550
WAVELENGTH , NM

of Cr(VI) monitored spectrophotometrically is in agreement with the radiotracer results. However, not only is the absorbance much greater for the extraction from HCl but there is a fine structure to the spectrum which is not apparent in the aqueous phase Cr(VI) solutions or in the extracts from the other acids.

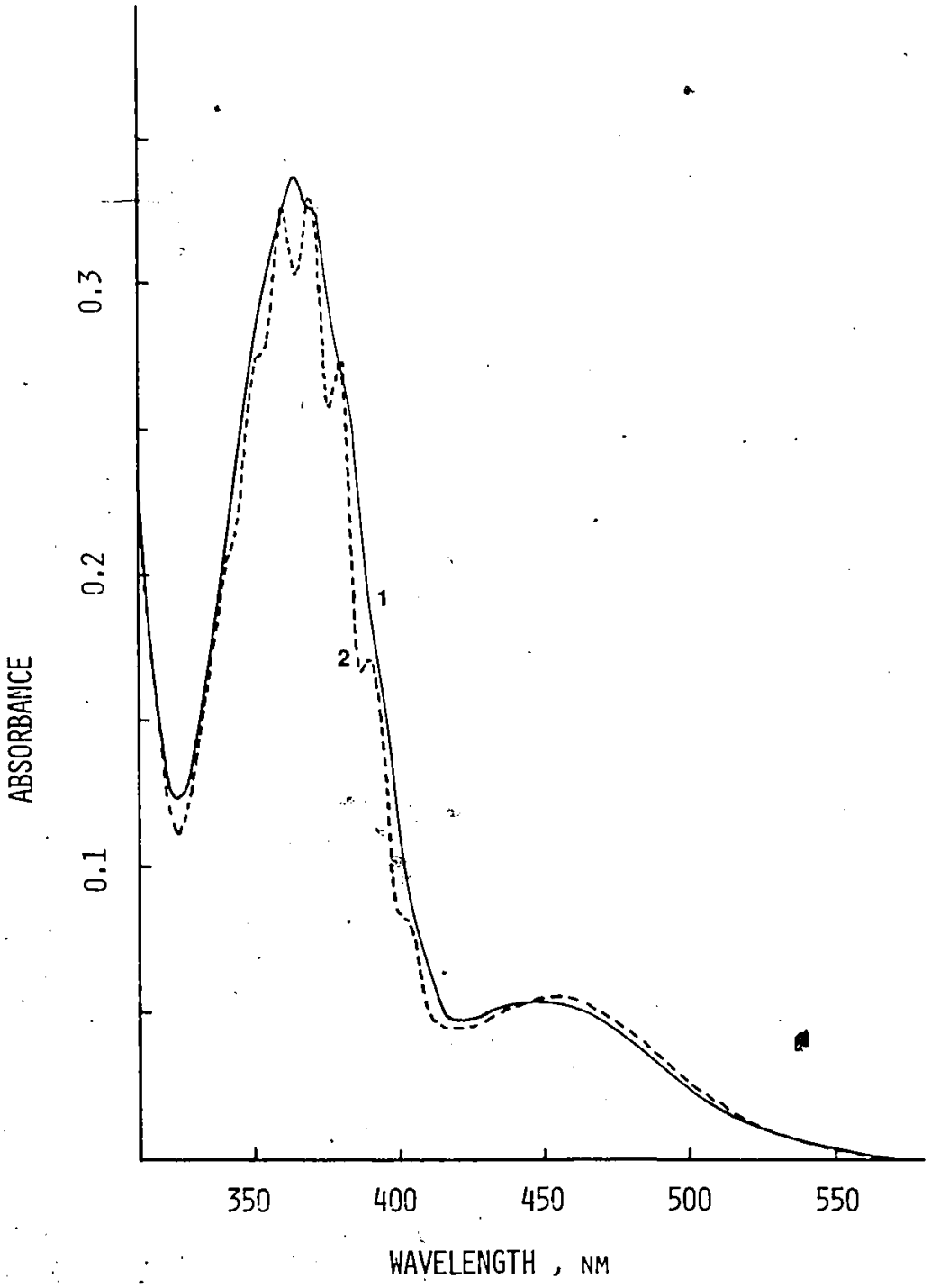
In a recent review[190] there is an indication of a growing interest in the examination of the vibrational fine structure for inorganic compounds such as Cr(VI). But before trying to explain the spectrum for the extract of $Cr_2O_7^{2-}$ from HCl solutions in 0.10M DPPM/CH_2ClCH_2Cl additional experiments should be reported. First, it was confirmed that the form of Cr(VI) initially introduced into the HCl solution made no difference - the behavior of Na_2CrO_4 and $KCrO_3Cl$ were identical to that of $K_2Cr_2O_7$. Extraction by 0.10M DPPM in CH_2Cl_2 and $CHCl_3$, while not quite as efficient as diluents as CH_2ClCH_2Cl, provided similar spectra. Figure 4.19 depicts the extraction of Na_2CrO_4 by 0.10M DPPM/CH_2Cl_2. There is little evidence of fine structure in the absorption band of Cr(VI) in the aqeuous HCl solution. After extraction into the organic phase the spectrum exhibits fine structure just as did the extract into CH_2ClCH_2Cl. Each absorption maximum occurs at the same wavelength in either diluent. The only difference is that in the extraction of the 13.3 ppm CrO_4^{2-} sample the maximum absorbance was 0.344 in CH_2ClCH_2Cl compared to 0.329 in CH_2Cl_2 at 364 nm.

The vibrational fine structure is not observed in aqueous solutions, possibly because of hydrogen bonding, but has been observed if the Cr(VI) is in an appropriate matrix. Thus, most studies involve the examination of single crystals at cryogenic temperatures[190] or

Figure 4.19

The spectra of 13.3 ppm CrO_4^{2-}

1. in an aqueous solution of 1 M HCl
2. in the organic phase after extraction by 0.10 M DPPM/CH_2Cl_2


ABSORBANCE
0.1
0.2
0.3
1
2
350
400
450
500
550
WAVELENGTH , NM

specially synthesized complexes in aprotic solvents.[191] The easy access to such spectra by a simple DPPM extraction could prove of interest to spectroscopists.

According to Bartecki et al.[192] only ions having a full C3v symmetry, such as the CrO_3Cl^- ion, exhibit such a well developed vibrational structure of the electronic bands related to the symmetric vibration ν_s Cr-O. The vibronic band for such Cr(VI) species consists of 5 - 9 members and its Franck-Condon absorption maximum depends on the type of solvent. The average distance between vibrational members equals about 760 cm^{-1}.

The Cr(VI) complex extracted by DPPM into CH_2ClCH_2Cl or CH_2Cl_2 exhibits 7 members which are clearly identifiable (Figure 4.18 and 4.19). Using the approach taken by McCain[193], when examining the inductive effects and Franck-Condon shifts in the visible spectra of substituted chromate ions, it is possible to assign each absorption maximum to a vibrational progression. The average $0 \rightarrow 0$ transition energy, ν_{oo}, is 25,100 cm^{-1} (398 nm) in most solvents with the CrO_3Br^- ion.[193] This should correspond to the 397 nm absorption in the Cr(VI) extract in DPPM/diluent. Table 4.10 lists the measured center absorptions and an estimate of the vibrational spacings for the transitions assigned according to this approach.

In this system ν_{max} occurs near ν_{03} (Figures 4.18 and 4.19). This is what would be expected if the Cr(VI) species in the extract is indeed CrO_3Cl^-.[193] The vibrational spacings are also consistent with expectations for CrO_3Cl^-,[190] albeit the data does not permit the resolution expected if the focus of research were spectroscopic in nature.

Table 4.10

Assigned transitions, measured center absorptions and estimated vibrational spacings for the Cr(VI) extract from HCl solutions into 0.10M DPPM/diluent.

Assignment	Absorption wavelength		Vibrational spacing	
	nm	(cm^{-1})	nm	(cm^{-1})
0 → 0	397.0	(25,190)		
			11.9	(780)
0 → 1	385.1	(25,970)		
			10.9	(750)
0 → 2	374.2	(26,720)		
			10.2	(750)
0 → 3	364.0	(27,470)		
			9.7	(750)
0 → 4	354.3	(28,220)		
			8.3	(680)
0 → 5	346.0	(28,900)		
			8	(680)
0 → 6	338	(29,590)		

Since the extraction of Cr(VI) from H_2SO_4 solutions is not like that from HCl solutions, both in terms of the extent and the resulting spectrum, it seems probable that the species extracted is different. It is known that H_2CrO_4 does not show resolved vibrational structure but CrO_3OH^- should.[193] Could CrO_3OH^-, if extracted, form a complex with the $DPPMH^+$ which effectively resulted in $DPPMH_2CrO_4$ and a destruction of the C3v symmetry? Alternatively, a S containing complex could be extracted or, as in the case with aqeuous solutions, the vibrational fine structure could be destroyed.

In addition to supporting the suggestion that CrO_3Cl^- is extracted by DPPM/diluent the spectral examinations of the system may be used to estimate the distribution ratio. This is not possible with much accuracy when D is very large since the absorption in the aqueous phase

after extraction is so negligible. However, as an example, when 0.010M DPPM/CH_2Cl_2 was used as the extractant the spectral measurements for the extraction of a 20ppm Cr(VI) solution in 1M HCl indicated that D = 14.7 ± 1. This compared favorably with the radiotracer estimate of D = 13.3 ± 1 for the same solution (Figure 4.8). While such spectrophotometric estimations of D corroborated the radiotracer results they were not used extensively.

The potential for the use of this extraction system in the analysis of Cr(VI) was also explored briefly. This will be mentioned in Section 4.2.6.

Infrared Spectra

Conventional infrared examinations of the DPPM/diluent extracts from the aqueous acidic solutions did indicate that there were regions between 400 - 4000 cm^{-1} where the % transmission changed from that of the DPPM/diluent solution alone. Of the most interest were the the extracts from HCl solutions. There were changes near 1600 cm^{-1}, 2000 cm^{-1} and 2500 cm^{-1} that warranted detailed investigation. When Cr(VI) was present and extracted, absorption occurred near 430 cm^{-1} and in a broad region between 800 cm^{-1} and 1000 cm^{-1}. It was decided that the application of Fourier transform infrared (FT-IR) techniques could better delineate the regions of interest. The following results, depicting the infrared activity in the organic extracts, are based on examinations by FT-IR.

To illustrate both the advantages and limitations of the FT-IR investigation undertaken a few direct spectra will be represented.

Since 0.10M DPPM/CH_2ClCH_2Cl is the best extraction vehicle for Cr(VI) the solution spectra of this system are depicted. From Figure 4.20a) it can be seen that the diluent CH_2ClCH_2Cl leaves few clear windows. Figure 4.20b) depicts the spectrum of 0.10M DPPM/CH_2ClCH_2Cl with CH_2ClCH_2Cl as the background and therefore subtracted out. While this spectrum for DPPM compares favourably with the Sadtler Standard Spectrum[194] of DPPM in a KBr wafer it can be seen that there are regions where there is considerable "noise" due primarily to the solvent. The extent to which this problem can be overcome will dictate the value of spectral information in these narrow regions.

As has been shown, the extraction of Cr(VI) from HCl solutions is excellent, from H_2SO_4 is limited and from other acids is negligible. Direct titration data indicates that HCl is partially extracted by DPPM/CH_2ClCH_2Cl but H_2SO_4 remains essentially in the aqueous layer. Does FT-IR of the extracts shed any light on these observations? Figure 4.20c) depicts the spectrum for the HCl extraction. While there is a general decrease in transmittance there are particular regions which stand out: 3675.7, 3591.1, 3440, 2414, 2048.0, 1977.5, 1611.1, 1540.7 cm^{-1}. For the H_2SO_4 extraction, Figure 4.20d), these regions are: 3675.7, 3591.1, 3450, 1600 cm^{-1}. Obviously, there are four regions in common for the acid extracts as well as several completely different absorption regions for the HCl situation.

Interpretation of these results may be better completed by switching to the absorbance mode and applying direct computer manipulation of the stored spectra. Further, since with the diluents $CHCl_3$, CH_2Cl_2 and CH_2ClCH_2Cl the extractions are similar it should not

Figure 4.20 a)

FT-IR spectrum of CH_2ClCH_2Cl in the transmittance mode.

Note: Spectra obtained from the Nicolet 7199 FT-IR analysis are direct photoreductions and reflect the manufacturers choice of format and labelling. Wavenumbers are in cm^{-1}.

Figure 4.20 b)

FT-IR spectrum of 0.1 M DPPM/CH_2ClCH_2Cl in the transmittance mode with CH_2ClCH_2Cl as the reference background.

Figure 4.20 a)

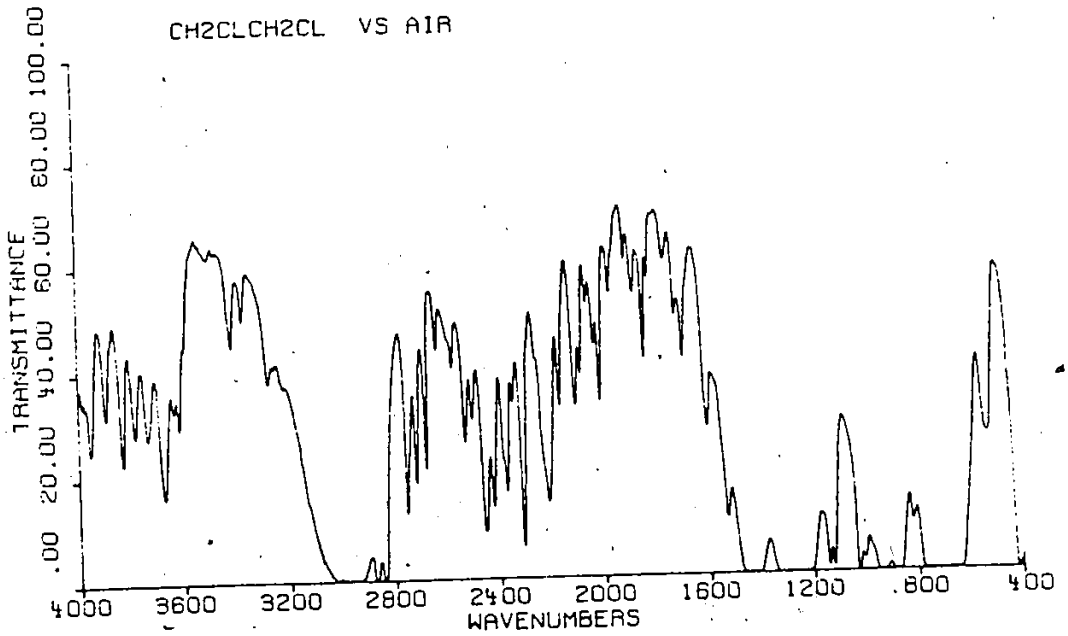


Figure 4.20 b)

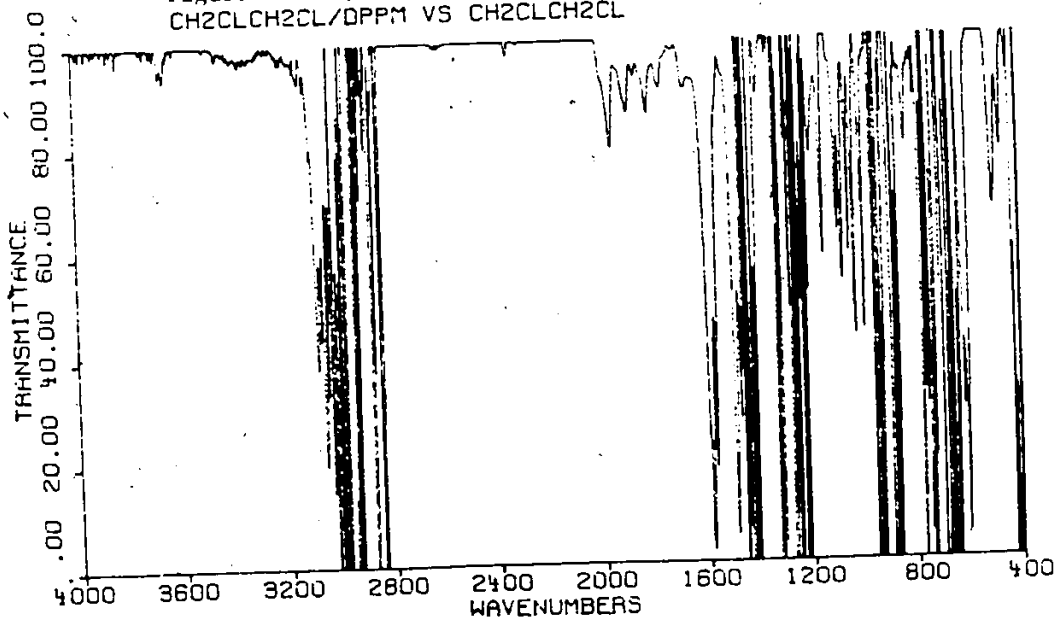


Figure 4.20 c)

FT-IR spectrum of the organic phase after the extraction of HCl from the aqueous phase by 0.1 M DPPM/CH_2ClCH_2Cl. The spectrum is recorded in the transmittance mode with CH_2ClCH_2Cl as the reference background.

Figure 4.20 d)

FT-IR spectrum of the organic phase after mixing 0.1 M DPPM/CH_2ClCH_2Cl with an equal volume of 1 N H_2SO_4. The spectrum is recorded in the transmittance mode with CH_2ClCH_2Cl as the reference background.

Figure 4.20 c)

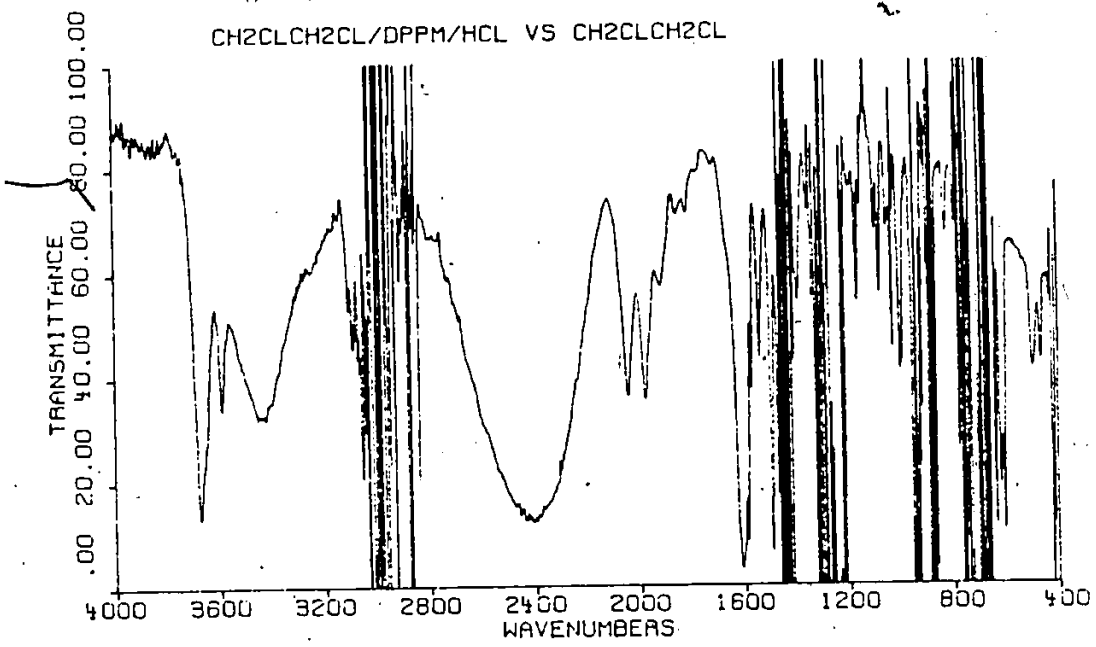
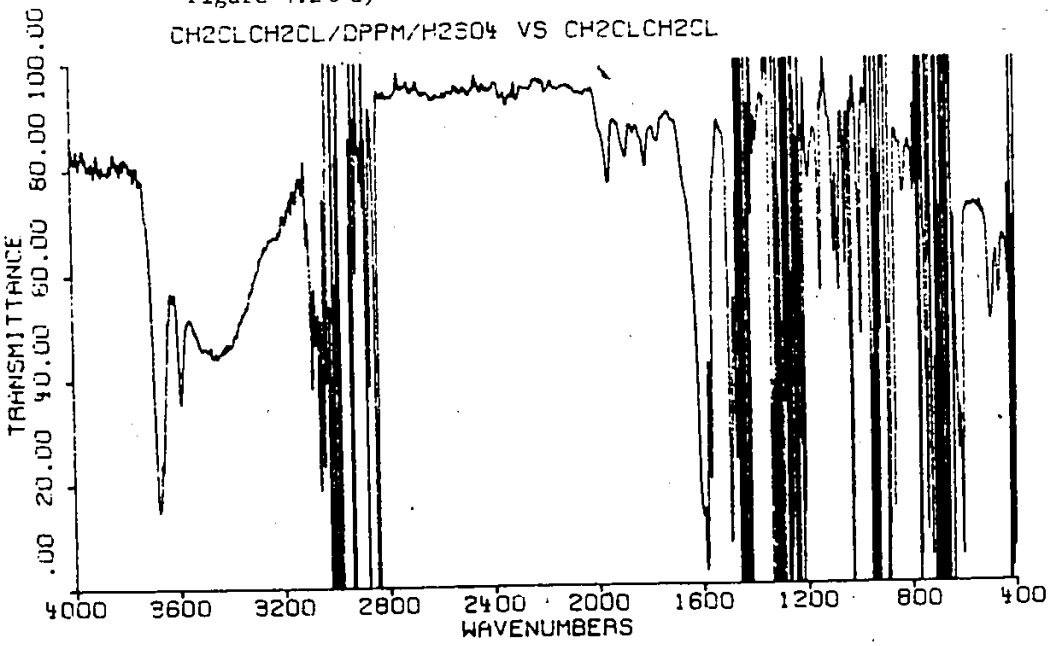


Figure 4.20 d)



matter which is used in the initial study. As it turns out there are some advantages in using CH_2Cl_2 - not only does it exhibit diluent effects intermediate between the other two diluents but it also leads to less spectral impairment in certain regions of interest. A 0.02M DPPM/CH_2Cl_2 extraction provided the essential information yet was technically easier to work with than a 0.10M solution.

Certain absorptions are common for extractions from all aqueous solutions. It was suspected that these were water bands. As illustrated in Figure 4.21a) and Figure 4.21b) these are indeed due to water with the natural solubility of water in the organic diluent being the cause, not any extraction by DPPM. In CH_2Cl_2 these sharp signals occur at 3689.8 cm^{-1}, 3598.2 cm^{-1} and 1604.1 cm^{-1}, with a broad signal near 3450 cm^{-1}. There is but a modest solvent dependence, cf, Figure 4.20c) and d).

According to the literature[195,196] the absorption centering near 3450 cm^{-1} and the associated two sharp maxima are due to the symmetric (ν_1) and antisymmetric (ν_3) valence vibrations or O-H stretching plus the first overtone of the bending vibration ($2\nu_2$). The literature value of 1645 cm^{-1} for liquid water is attributed to the scissors vibration (ν_2) or H-O-H bending. Since in these extraction systems the signal always occurs closer to 1600 cm^{-1} it could be suggested that the water is isolated to some extent as in water vapour where this maximum occurs at 1595 cm^{-1}. There is also evidence of the libration band (ν_L), the broad band extending anywhere from 300 cm^{-1} to 900 cm^{-1}. Any association band (ν_A) near 2125 cm^{-1} for water is too weak to be characterized.

Figure 4.2 1 a)

FT-IR spectrum of CH_2Cl_2 saturated with water. The spectrum is in the absorbance mode with CH_2Cl_2 as the reference background.

Figure 4.2 1 b)

FT-IR spectrum of the organic phase after mixing 0.02 M DPPM/CH_2Cl_2 with water. The spectrum is in the absorbance mode with the same organic phase in the dry form used as the reference background.

Figure 4.21 a)

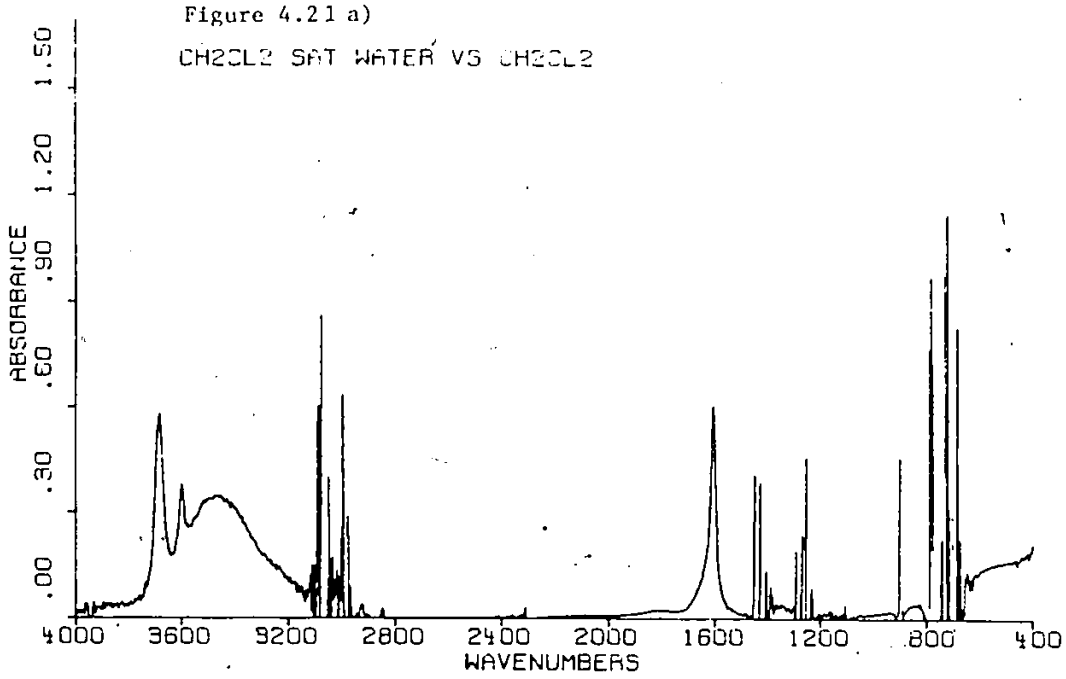
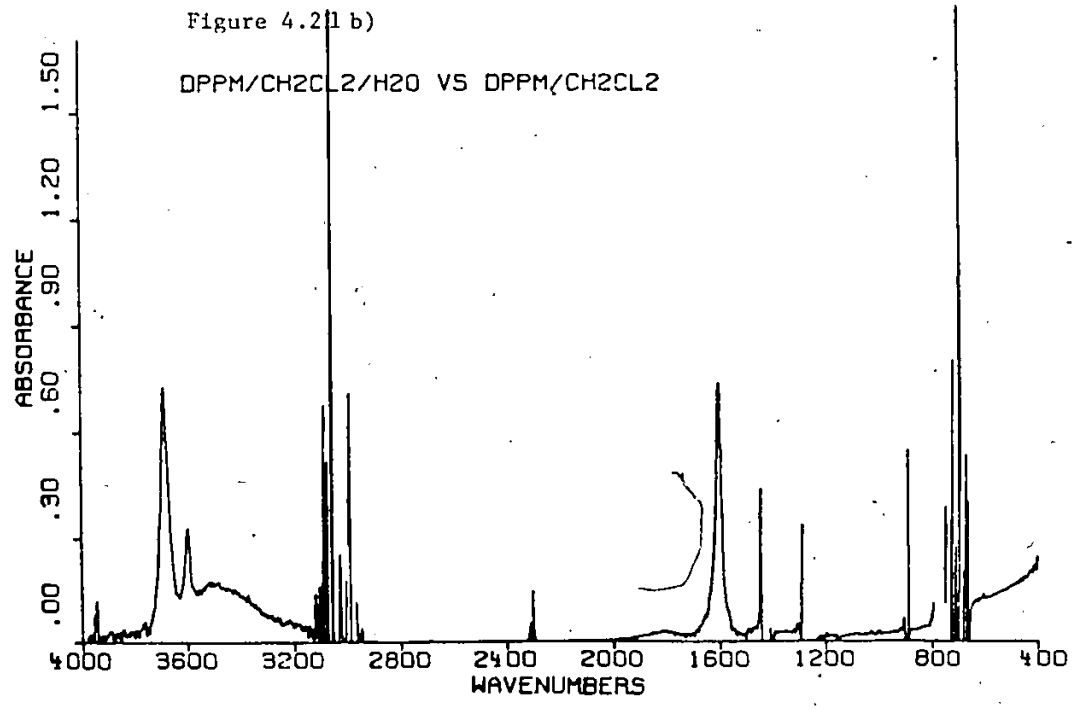


Figure 4.21 b)



The introduction of an acid to the system has interesting consequences. It is of value to compare the spectra for the acids HCl and H_2SO_4, Figures 4.22a) and 4.22b), each of these being important to Cr(VI) extraction. The simpler spectrum of H_2SO_4 is almost identical to that observed when water is placed in contact with DPPM/CH_2Cl_2. With HCl there are a number of additional absorptions at 2421 cm^{-1}, 2040.0 cm^{-1}, 1977.5 cm^{-1} and 1537.3 cm^{-1}. The extracts from both $HClO_4$, Figure 4.22c), and HNO_3, Figure 4.22d), show absorption at these same positions but the spectrum from H_3PO_4, Figure 4.22e) does not.

How are these new absorption bands, evident in the spectra from the HCl, $HClO_4$ and HNO_3 extractions, accounted for? Since they are not particularly specific to the acid they must be due to some involvement of the proton alone in the organic phase. They do not occur in the extracts from H_2SO_4 or H_3PO_4 because, as has been shown by two phase titrations, these acids are not extracted. The changes in the dielectric constant or hydrogen bonding ability of the diluent may be responsible for the slightly shifts in the band maxima. Only with the broad maxima at about 2414 cm^{-1} in CH_2ClCH_2Cl, 2421 cm^{-1} in CH_2Cl_2 and 2463 cm^{-1} in $CHCl_3$, is there a trend that parallels the diluent properties. At this time an assignment of the vibrations responsible for these bands is not possible, but they are probably due to the DPPM - H^+ bond. How this protonation affects the rest of the molecule and how the formation of the different possible ion-pairs, $DPPMH^+ - X^-$, contributes to the overall absorptions is not obvious.

Some additional information may be obtained from these spectra. It is apparent from Figure 4.22c) that there is an absorption near

Figure 4.2 2a)

FT-IR spectrum of the organic phase after mixing equal volumes of 0.02 M DPPM/CH_2Cl_2 with an aqueous solution of 1 M HCl. The spectrum is recorded in the absorbance mode with the original organic phase used as the reference background.

Figure 4.2 2b)

FT-IR spectrum of the organic phase after mixing equal volumes of 0.02 M DPPM/CH_2Cl_2 with an aqueous solution of 1 N H_2SO_4. The spectrum is recorded in the absorbance mode as in a).

Figure 4.22 a)

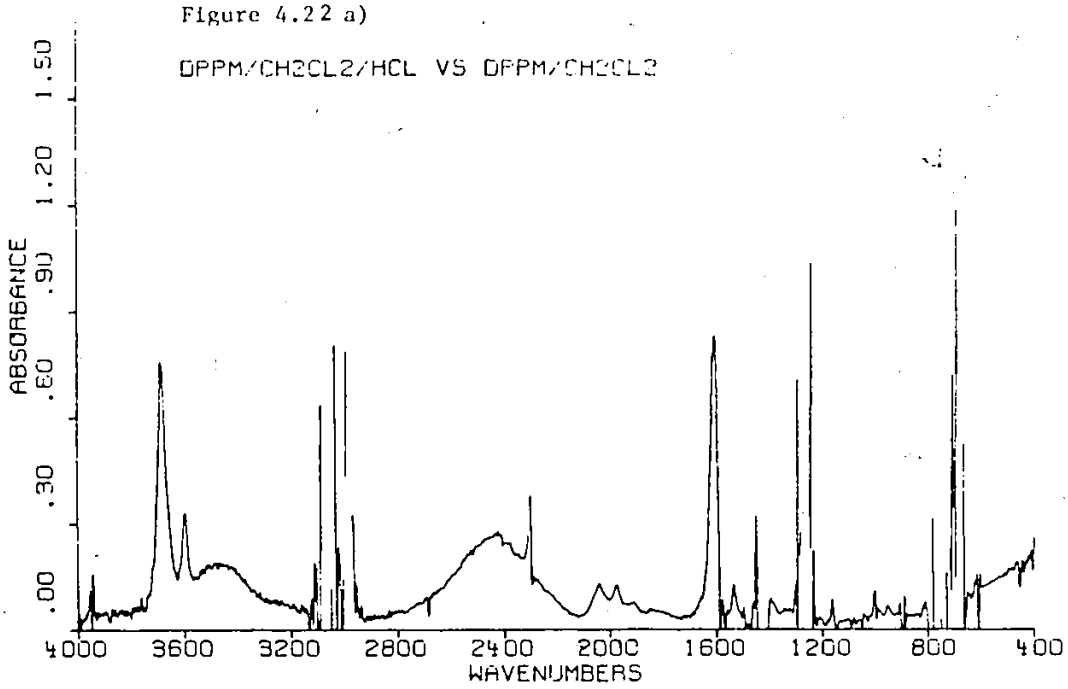


Figure 4.22 b)

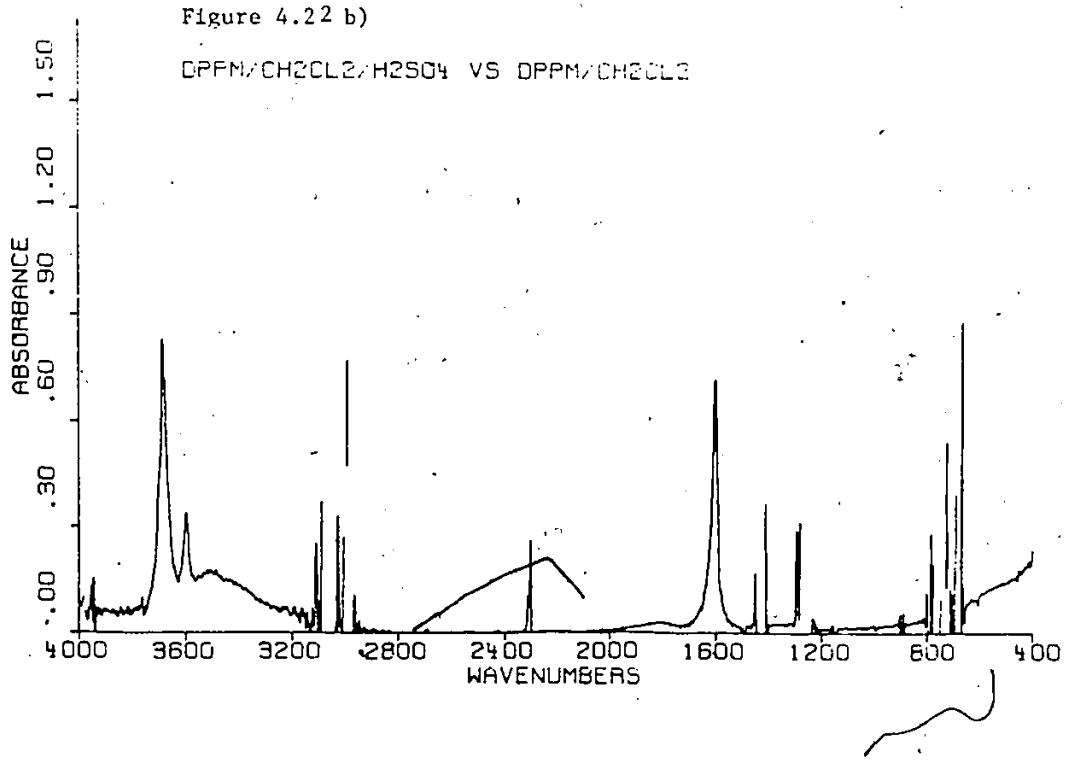


Figure 4.22 c)

FT-IR spectrum of the organic phase after mixing equal volumes of 0.02 M DPPM/CH_2Cl_2 with an aqueous solution of 1 M $HClO_4$. The spectrum is recorded as in a).

Figure 4.22 d)

FT-IR spectrum of the organic phase after mixing equal volumes of 0.02 M DPPM/CH_2Cl_2 with an aqueous solution of 1 M HNO_3. The spectrum is recorded as in a).

Figure 4.22 e)

FT-IR spectrum of the organic phase after mixing equal volumes of 0.02 M DPPM/CH_2Cl_2 with an aqueous solution of 1 N H_3PO_4. The spectrum is recorded as in a).

Figure 4.22 c)

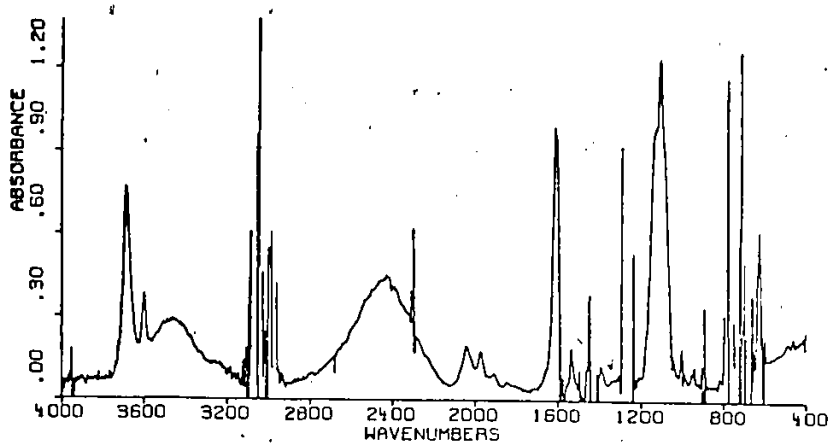


Figure 4.22 d)

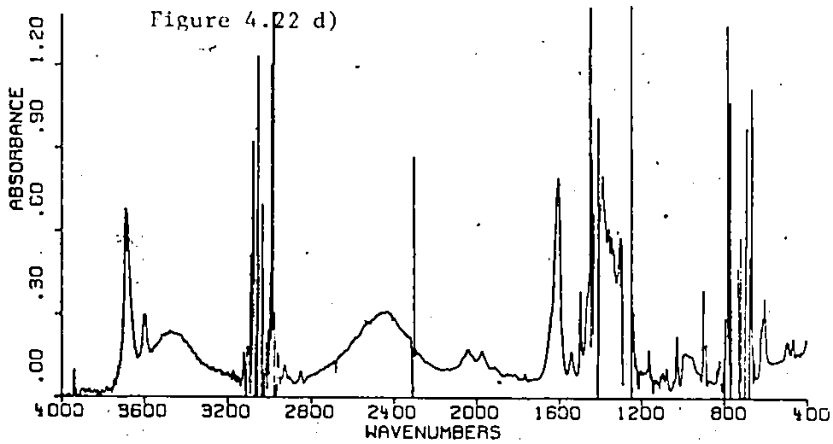
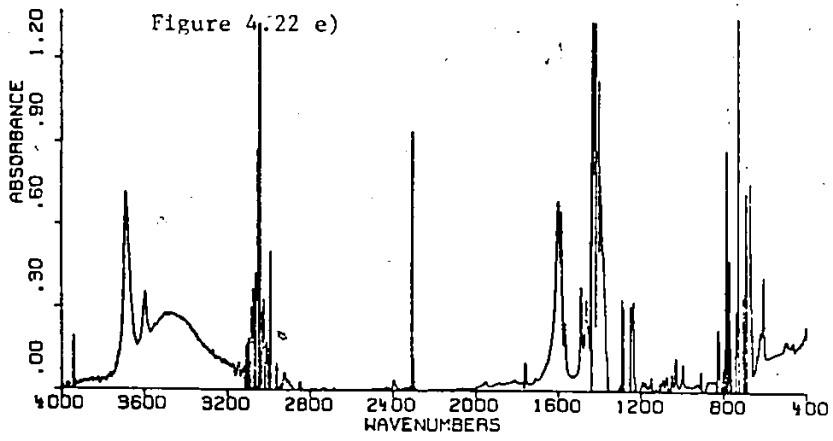


Figure 4.22 e)



1100 cm^{-1} due to the extraction of $HClO_4$ and from Figure 4.22d) an absorption near 1380 cm^{-1} due to the extraction of HNO_3. According to Nakanishi and Solomon[197] there are bands expected for ClO_4^- from 1100 - 1025 cm^{-1} and 650 - 600 cm^{-1} and for NO_3^- from 1380 - 1350 cm^{-1} and 840 - 815 cm^{-1}. The corresponding bands for SO_4^{2-} are from 1150 - 1055 cm^{-1} and for PO_4^{3-} are from 1100 - 1000 cm^{-1},[197] yet no such absorptions appear in Figures 4.22b) and 4.22e). This spectral evidence confirms that ClO_4^- and NO_3^- are extracted in the DPPM systems but SO_4^{2-} and PO_4^{3-} are not. As to the extraction of Cl^- by the protonated extractant in HCl solutions, the characteristic infrared band for HCl at 2840 cm^{-1} [198] cannot be located in any spectra. It is possible that in this region any absorption is obscured but it is more probable that HCl is not extracted as a molecular species. It also seems improbable the HCl_2^- is extracted to any extent. There are no characteristic absorptions at 1180 cm^{-1} and 1565 cm^{-1} for HCl_2^-,[198] albeit there is a weak absorption at 1167 cm^{-1}, Figure 4.22a) and 4.23a).

In the region below 1200 cm^{-1}, the absorptions in extracts from HCl solution may be examined in more detail, Figure 4.23a). There are no major absorptions that are not common to all extracted solutions - including those from H_2O, H_2SO_4, HNO_3, H_3PO_4 as well as $HClO_4$. In the spectrum from $HClO_4$, Figure 4.23b), there are at least two additional prominent absorptions. At 1110.9 cm^{-1} there is the peak with two left shoulders and at 624.7 cm^{-1} there is the signal that shows up in no other acid extracts. These bands must be attributed to ClO_4^- and are a clear indication that this anion is extracted readily.

In examining the extraction of Cr(VI) from 1M HCl solutions by

Figure 4.23 a)

FT-IR spectrum from Figure 4.22 a) expanded from 400 - 1200 cm^{-1}.

Figure 4.23 b)

FT-IR spectrum from Figure 4.22 c) expanded from 400 - 1200 cm^{-1}.

Figure 4.23 a)

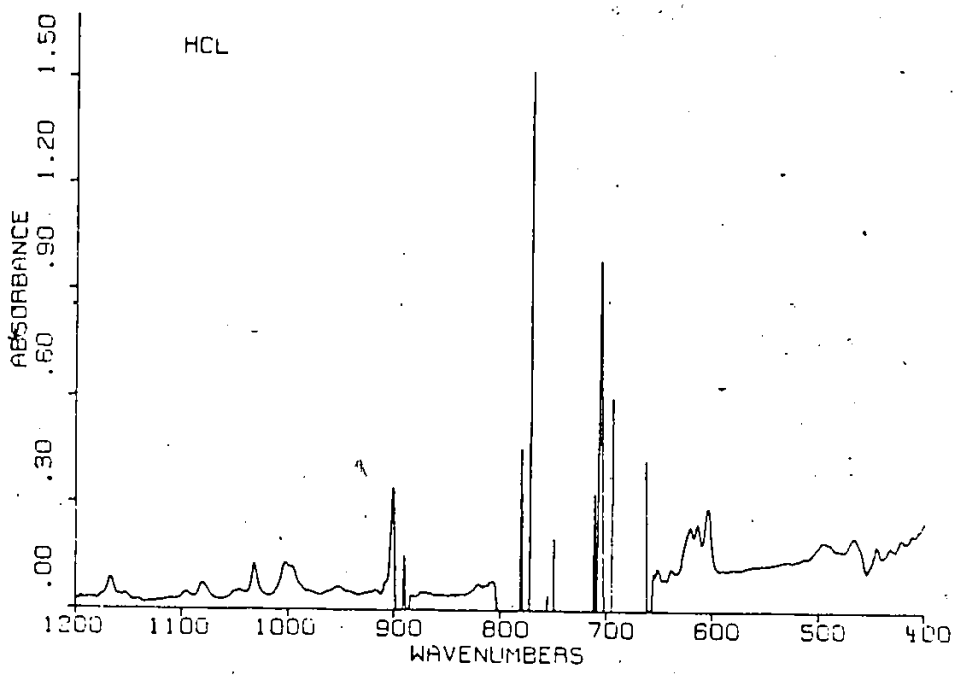
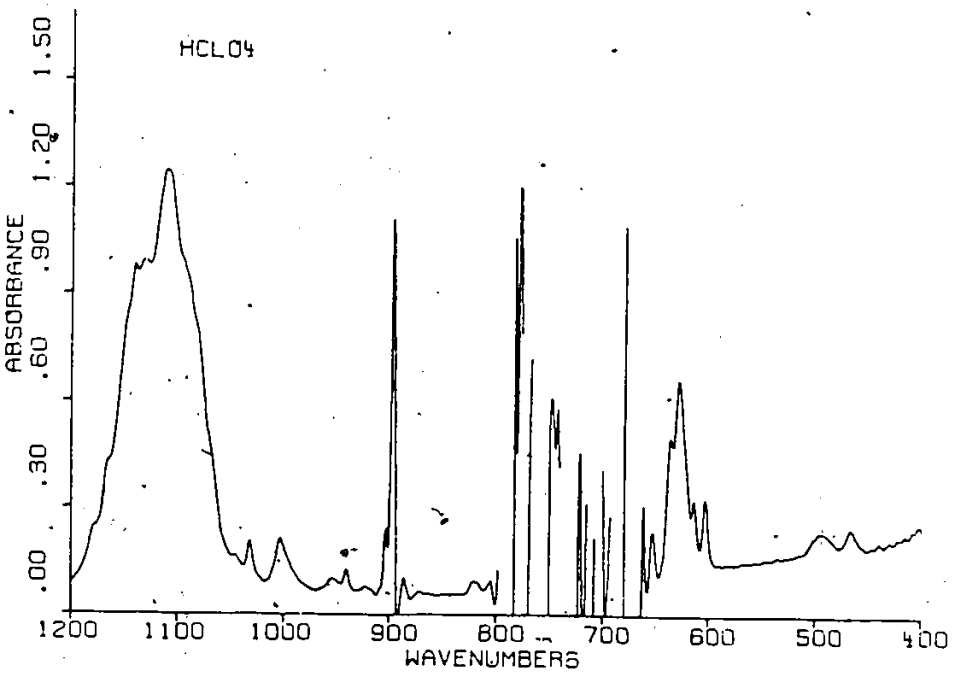


Figure 4.23 b)



0.10M DPPM/diluent it was recognized that the source of the Cr(VI), whether it be $(NH_4)_2CrO_4$, $K_2Cr_2O_7$ or $KCrO_3Cl$, made no different in the spectra. It seems most probable that the equilibria established in the aqueous phase leads to extraction of identical species from all of these salts. It should also be remembered that while the extractions and separations are clean for the three diluents used, the extraction by 0.10M DPPM/$CHCl_3$ is not nearly as good as the others. Further, for the $CHCl_3$ diluent, although reasonable spectra may be obtained there is some color change in the extract after irradiation in the IR solution cell, which is interpreted as a break down of the complex under the experimental conditions.

Background corrections become more suspect with the 0.10M DPPM/diluent extracts as well. Slight shifts in maxima, the partition of the DPPM between each phase and consequent loss from the organic system, changes in solvation, etc. may all contribute to these complications.

Only the Cr(VI) spectra with diluent CH_2ClCH_2Cl are illustrated in full. Although the spectrum indicating the difference in the presence of Cr(VI) is illustrated in Figure 4.24a) it is of value to compare Figure 4.24b) with Figure 4.20c), even though that spectrum is in transmittance, to see the overall effect. There are a few regions with significant changes. The absorbance of DPPM from HCl near 2414 cm^{-1} has been shifted to near 2600 cm^{-1} and it, along with the other bands attributed to the protonation of DPPM, has increased moderately in absorbance. The absorbance at 1611 cm^{-1} has increased quite significantly. It was initially attributed to water but the other water

Figure 4.24 a)

FT-IR spectrum for the organic phase after mixing equal volumes of 0.1 M DPPM/CH_2ClCH_2Cl with an aqueous solution of 1 M HCl containing 0.01 M Cr(VI). The spectrum is recorded in the absorbance mode with the same solution without th Cr(VI) as the reference background.

Figure 4.24 b)

FT-IR spectrum as in a) with CH_2ClCH_2Cl used as the reference .

Figure 4.24 a)

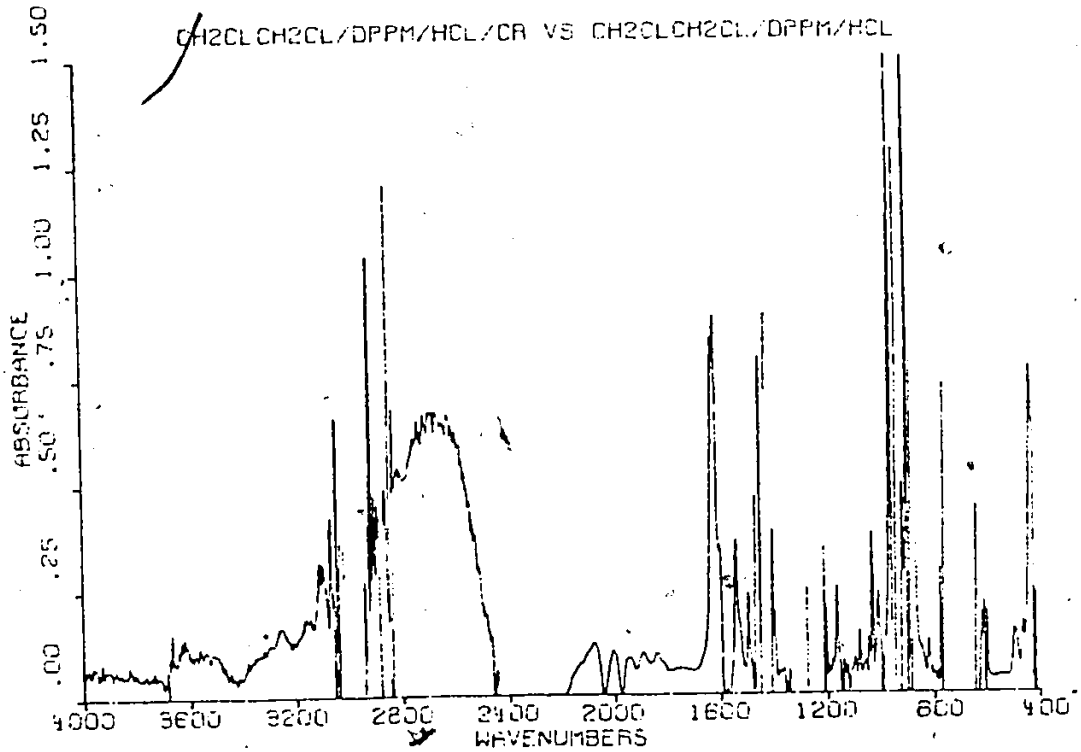


Figure 4.24 a)
expanded

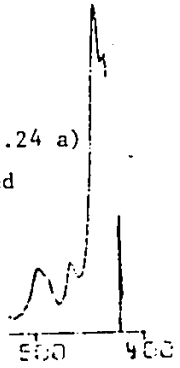
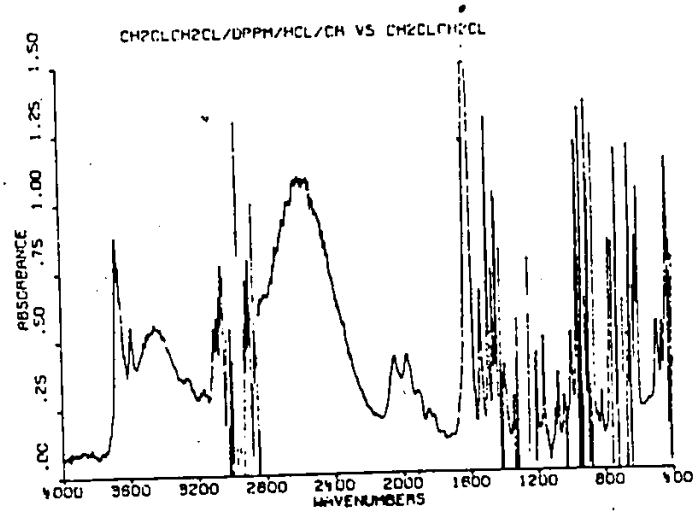


Figure 4.24 b)



bands have changed little. It is probable that the band has not only the absorption contribution from water but also from the protonation phenomenon. A contribution from the protonation could explain why with the $HClO_4$ extract this band appears abnormally strong as well. This observation is in keeping with a report by Bartecki et al.[191] In the examination of Cr(VI) compounds with aminophosphoric esters they attributed such bands to NH^+, actually NH_2^+ in this case, in the organic structure. It seems possible that the NH^+ in DPPM would behave in a similar manner. Notice also that at 3280 cm^{-1} there is a difference signal of some magnitude. Bartecki et al.[191] list a strong N-H stretching for this region, although it must be remembered that in this extract OH stretching could contribute as well. As to why there would be an increased protonation in the presence of Cr(VI) is unclear. It could reflect the fact that Cr(VI) is expelled from the aqueous phase in an anionic form quite readily. Of course protonation can occur only with an accompanying anion because of charge balance requirements. Such a phenomenon may only become apparent at the high Cr(VI) concentrations employed in the IR analysis and at trace levels need not effect the equilibrium conditions established by the acid alone.

Most of the other unambiguous bands can be accounted for in terms of the vibration modes for the Cr(VI) complex extracted. Absorptions of particular significance occur near 950 cm^{-1} and 440 cm^{-1} (see the expanded insert of Figure 4.24a)). Since these show up with all diluents, although at slightly different wave numbers for the maximum absorbance, it is most reasonable to inspect this information as presented in Table 4.11a). To be certain of assignments a more complete

Table 4.11.

a). Infrared absorption bands attributed to Cr(VI) in the extracts from 1 M HCl into DPPM/diluent.

Infrared bands for diluent (cm^{-1}).			Approximate description
$CHCl_3$	CH_2Cl_2	CH_2ClCH_2Cl	
438.4 m	438.4 m	438.4 s	ν (CrCl)
747 m	748 s		ν_{as}(CrOCr)?
900 s	843 s	902 s	ν_s (CrO)
941 s	941 s	946 s	
952 s	951 s		ν_{as}(CrO),
958,961 s	961 s	963 s	
965 s		969 s	

b). Infrared absorption bands attributed to Cr(VI) in the extracts from 1 N H_2SO_4 into DPPM/diluent.

Infrared bands for diluent (cm^{-1}).			Approximate description
$CHCl_3$	CH_2Cl_2	CH_2ClCH_2Cl	
700 s	708 s		ν_{as}(CrOCr)?
736 m	738 s	739 s	
886 m	893 w	899 s	ν_s(CrO)
904 m	904 w	904 s	
926 m		922 m	
	932 m		ν_{as}(CrO)
940 s	941 ms		
949 s	949 ms		
	961 m	965 s	

Note: s = strong, m = moderate, w = weak

References used (199, 200, 201, 202) may include some assignments made by Raman as well as infrared spectroscopic methods.

examination, requiring variations in the concentration of DPPM, acid and Cr(VI), would be necessary to optimize the Cr(VI) signals. Since exact absorbance values are questionable the absorbance is listed only qualitatively in Table 4.11a).

Before elaborating on the absorptions ascribed to Cr(VI) in extracts from HCl it could be useful to examine those from H_2SO_4. These extracts from H_2SO_4 were difficult to deal with and the cells deteriorated quite quickly. Decomposition under experimental conditions was obvious, most noticeable with extracts into $CHCl_3$. Nevertheless, the total spectrum in CH_2ClCH_2Cl is depicted in Figure 4.25. When compared to Figure 4.20d) there is a noticeable enrichment in the broad absorption near 2600 cm^{-1}, just as was observed in the extractions of Cr(VI) from HCl solutions. Likewise the 1611 cm^{-1} band has increased. Further comparisons may be made near the 2040 - 1978 cm^{-1} doublet and the 1537 cm^{-1} singlet; these absorptions having shown up in extracts from some acids but not H_2SO_4 itself. Again, the bands near 1100 cm^{-1} and 630 cm^{-1} appear in a difference spectrum, but remembering that they occur also with extracts from pure $HClO_4$ they cannot be attributed to stretching or bending modes within the Cr(VI) complex. Those remaining signals which are probably due to Cr(VI) alone are listed in Table 4.11b).

From Tables 4.11a) and 4.11b) it is apparent that extractions from HCl lead to a significant absorbance at 438.4 cm^{-1} which is absent in extractions from H_2SO_4. One direct means of illustrating this may be seen in Figure 4.26. Although the extraction of Cr(VI) is in general better using HCl, as evidenced by the greater absorbances near 950 cm^{-1},

Figure 4.25

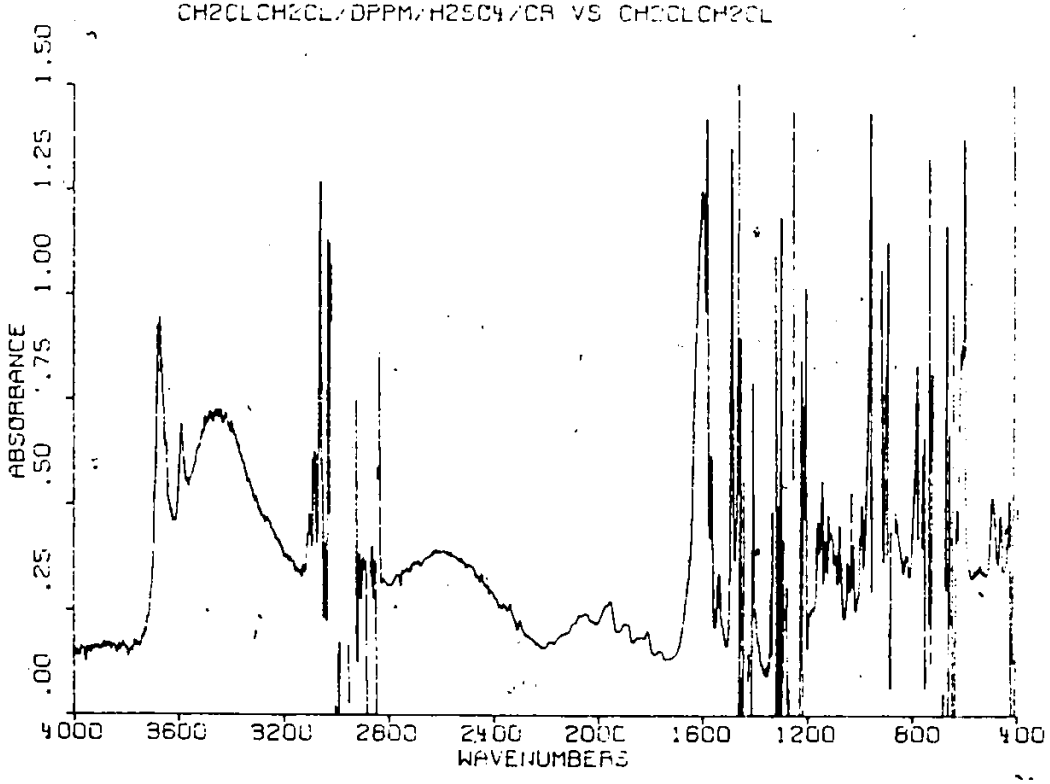
FT-IR spectrum of the organic phase after mixing equal volumes of aqueous 1 N H_2SO_4 solution containing Cr(VI) with 0.1 M DPPM/ CH_2ClCH_2Cl. The spectrum is recorded in the absorbance mode with the reference background CH_2ClCH_2Cl.

Figure 4.26

FT-IR difference spectrum of the extract from 1 M HCl and 1 N H_2SO_4 using the same 0.1 M DPPM/$CHCl_3$ extractant and with the same Cr(VI) originally in the aqueous phase.

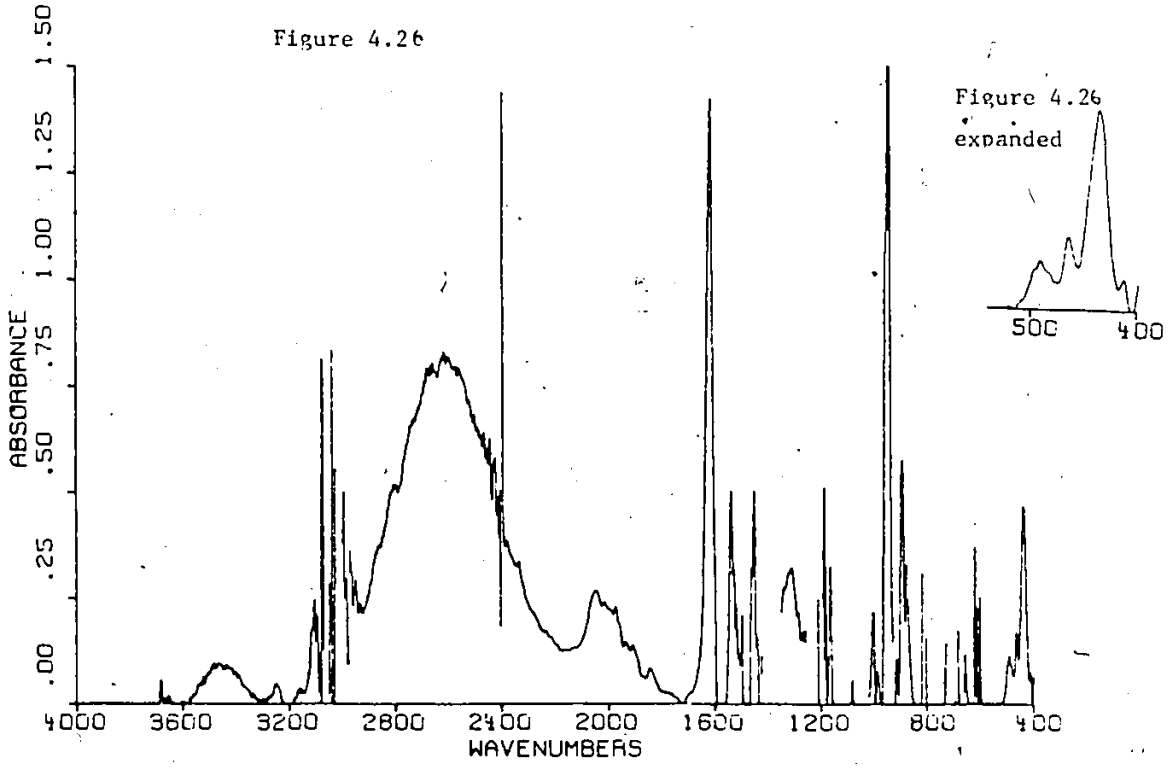
Figure 4.25

CH2CLCH2CL/DPPM/H2SO4/CR VS CH2CLCH2CL



CHCL3/DPPM/HCL/CR VS CHCL3/DPPPM/H2SO4/CR

Figure 4.26



there is the signal at 438.4 cm^{-1} from HCl which is not present in the H_2SO_4 extraction. If this signal is due to Cr-Cl vibrations it can be concluded that Cr(VI) is extracted mainly as CrO_3Cl^- from HCl solutions. Some extraction may occur as $HCrO_4^-$, or at the high Cr(VI) concentrations even $HCr_2O_7^-$, and it may be that from H_2SO_4 these forms alone are extracted or specific species such as $CrO_3HSO_4^-$ could be present.

A comparison of the extraction from HCl into the three diluents indicates that there may be differences in both amount and kind of Cr(VI) present. The absorption due to the Cr-Cl vibration, while never as large as that for the Cr-O vibrations, is progressively more significant as the dielectric constant of the diluent increases. This suggests that complexes in addition to CrO_3Cl^- may be extracted, particularly in the less polar diluents.

An examination of the spectra for the extracts of Cr(VI) by 0.02M DPPM/CH_2Cl_2 in the far infrared region, 200 - 500 cm^{-1}, provided little additional information. Extraction of water increasingly interfered with the examination as the wavenumbers decreased. However, there was an absorption maximum with a series of peaks between 375 and 384 cm^{-1} in the extract from HCl. The O - Cr - O bending vibration in $Cr_2O_7^{2-}$ and CrO_3Cl^- has been reported at 365 cm^{-1} and may account for the observed bands.[199,200] These bands did not occur in the extracts from H_2SO_4.

Summation

The spectral examinations of both the acid and Cr(VI) extractions by DPPM/diluent provide general support for the extraction model. In the UV-visible region the protonation of DPPM is as predicted from the titration data at the much higher concentrations of the working systems. The Cr(VI) extracted from HCl solutions is probably CrO_3Cl^- as evidenced by the interesting spectral fine structure, although other ions with C3v symmetry cannot be completely ruled out. Certainly there is a spectral difference between the extracts from HCl and H_2SO_4 which, along with other extraction evidence, suggests that the species which ends up in the organic phase is quite different in the two cases. This is further confirmed by the IR examinations. Here there is clear support for the extraction of CrO_3Cl^- from the HCl solutions.

Attempts to confirm the infrared work by Raman spectroscopy were unfortunately of little success. There was a decomposition problem when extracts of Cr(VI) were placed in the laser beam. The rotating cell technique advocated by Carter and O'Hare[203] for Cr(VI) complexes subject to photochemical decomposition did overcome this problem but the absorption signals were not sufficiently clear to be assigned. The only band that could be attributed to Cr(VI) occurred near 900 cm^{-1}. This could not be used to distinguish between the various possible Cr(VI) complexes since it is probably due to the symmetric Cr-O vibration.[200,201]

Oxygen-17 nuclear magnetic resonance spectroscopy was also considered. Several Cr(VI) complexes have known ^{17}O chemical shifts[204] which could be used in their identification, but CrO_3Cl^- has not been

reported. Preliminary investigations using 1M Cr(VI) solutions in the aqeuous phase indicated that while this technique had some potential it could not be used with the extracts of lower Cr(VI) concentration without ^{17}O enrichment or extremely long running times on the instrumentation available.

4.2.5 Extraction of substances other than ordinary Cr(VI)

There was little concern that cationic Cr(III) would be extracted by DPPM/diluent from aqueous acidic solutions. Yet, the ability of the extraction system to separate Cr(VI) from Cr(III) was confirmed and the separation factor in the effective diluents was found to be as reported by Iqbal and Ejaz[74] in $CHCl_3$, ie. $\alpha = D_{Cr(VI)}/D_{Cr(III)} > 10^5$.

However, anionic Cr(III) complexes such as tris-oxalato Cr(III) have been extracted by several high molecular weight amines.[150,168] Effective extractions by triaurylamine in a number of dilents was possible with up to 0.1M H_2SO_4 and H_3PO_4 or up to 0.001M HCl but the complex was stripped from the organic phase by 0.1M $HClO_4$, HNO_3 or HCl.[150]

With DPPM/diluent the extraction of $Cr(C_2O_4)_3^{3-}$ was not achieved from solutions with HCl concentrations greater than 0.1M. Investigations at lower acid concentrations were not performed but at least there is no possible confusion in speciation of chromium from HCl solutions at acid concentrations in which the distribution ratio of Cr(VI) is near the maximum. In general, the separation and speciation of chromium by an extraction method, such as the one with DPPM, may be much more reliable than alternative coprecipitation or ion-exchange

methods. Using 0.10M DPPM/diluent and aqueous solutions of about 1M HCl the anionic Cr(VI) is cleanly separated from both cationic Cr(III) and anionic Cr(III) species of the oxalato type.

The extraction of Cr(VI) from HCl solutions in the presence of excess H_2O_2 was also examined. The study was not extensive but a summary of the results will be presented because there are some aspects of this work which deserve attention since they are germane to the extractions of the Cr(VI) species already mentioned.

A radiolabelling experiment conducted in the adopted manner indicated that the complex formed by Cr(VI) in 0.6M HCl in the presence of 0.5% H_2O_2 was extracted quickly and almost quantitatively. Using 0.10M DPPM/CH_2ClCH_2Cl the distribution ratio was estimated at D = 62. Ion-exchange procedures confirmed that the extracted ^{51}Cr was anionic. On the other hand, the ^{51}Cr in the aqueous phase, which built up as the two phases remained in contact, was cationic. The results were similar if Cr(VI) was first extracted in the absence of excess H_2O_2 and then the H_2O_2 was added later.

After having established that the extraction of the peroxychromic acid complex was possible at trace levels the Cr(VI) concentration was increased until an extraction was visible to the unaided eye. A more detailed spectrophotometric analysis indicated that the absorption maximum was at 570 nm. If the Cr(VI) was quantitatively extracted the molar absorption coefficient was estimated as 500 ± 10 M^{-1} cm^{-1}.

An examination of the literature indicates that the complex which forms rapidly in acidic aqeuous chromate solutions containing

H_2O_2, commonly called perchromic or peroxychromic acid, can be of two forms - a blue form at low pH values and a violet form when the pH is between 4 and 7.[205] Thus, blue diperoxychromium(VI), $CrO(O_2)_2.H_2O$, should predominate in the aqueous phase under the extraction conditions employed.

$$HCrO_4^- + 2H_2O_2 + H^+ \rightleftharpoons CrO(O_2)_2.H_2O + 2H_2O \qquad (4.25)$$

This complex has an absorption maximum at 580 nm with a molar absorption coefficient listed from 450[206] to 530 ± 40[207] M^{-1} cm^{-1}. At acid concentrations greater than about 0.1M there is a decrease in absorbance which has been attributed to the protonation of the oxo group.[207]

$$CrO(O_2)_2 + H^+ \rightleftharpoons Cr(OH)(O_2)_2^+ \qquad (4.26)$$

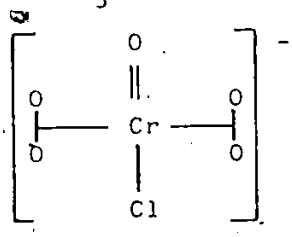
Witt and Hayes[205] have reported that at higher pH values the violet complex is formed according to

$$HCrO_4^- + 2H_2O_2 \rightleftharpoons CrO_5(OH)^- + 2H_2O \qquad (4.27)$$

This complex has an absorption maximum at 540 nm with ε = 510 M^{-1} cm^{-1}.

Were these the only possible peroxychromium(VI) complexes it would be difficult to account for the extraction. The essentially neutral $CrO(O_2)_2$ molecule, if present, should be distributed between the aqueous phase and organic phase even in the absence of DPPM. Extraction in the absence of DPPM did not prove practicable. Since DPPM acts as an extractant of anionic complexes it is more probable that the peroxychromium(VI) complex that forms the extractable ion-pair is indeed anionic. However, this is not likely to be $CrO_5(OH)^-$, for it does not form at the low pH values used. Further, the experimental absorption maximum of the extracted complex is not particularly close to that of 540 nm which is expected for $CrO_5(OH)^-$.

The extractable species considered most probable is the anionic chloroperoxy-complex of Cr(VI). Experimental evidence supports both the anionic nature of the extracted complex and an ease of formation from what is known to be CrO_3Cl^- extracted from HCl solutions. Tuck[208] has suggested that the complex which could be formed from CrO_3Cl^- by a substitution reaction would have the structure



In addition, this species better accounts for the extractions of the peroxychromic acid complexes studies by Sastri and co-workers[160,209] than can $CrO(O_2)_2$. In one study there was a definite acid dependence with extractions possible from HCl or H_2SO_4 but not $HClO_4$ into TnOA/benzene.[160] In an infrared examination of the ion association derivatives in the TnOA after extraction from HCl solutions there was an activity at 438 cm^{-1},[209] reminiscent of the Cr-Cl stretching absorption.

Such evidence tends to support the contention that in the DPPM extraction the anion involved is $CrO(O_2)_2Cl^-$. It is likely that this is formed by the peroxide reaction on CrO_3Cl^- and that there is retention of the Cr-Cl bond during the substitution reaction. Either CrO_3Cl^- or $CrO(O_2)_2Cl^-$ could be extracted initially but it is clear that in the presence of H_2O_2 the CrO_3Cl^- no longer exists and the product ultimately formed in the organic phase is an ion-pair such as $DPPMH^+$ $CrO(O_2)_2Cl^-$.

While the formation and extraction of the peroxychromic acid complex is too rapid to study by conventional means the decomposition of the extracted complex can be monitored radiometrically and

spectrophotometrically. This decomposition is much slower in organic extracts than in an aqueous solution. A recent report[207], based on stopped-flow techniques, represents the decomposition in an aqeuous solution as:

$$2CrO(O_2)_2 + 6H^+ \rightleftharpoons 2Cr^{3+} + 3O_2 + H_2O_2 + 2H_2O \quad (4.28)$$

This reduction, in a matter of seconds in an aqueous solution, contrasts markedly with the reduction in the DPPM/CH_2ClCH_2Cl extract which is measured in hours.

A radiometrically monitored reduction was done in parallel with the reduction in a similar extract of 10^{-3}M Cr(VI) prepared in the absence of H_2O_2. These extracts in 0.10 DPPM/CH_2ClCH_2Cl were continuously but gently mixed with twice the volume of a 1.2M HCl aqueous solution. Periodic determinations of the activity in an aliquot of each aqueous layer, reflecting the conversion to $^{51}Cr^{3+}$, were conducted over a duration of several days. The rates of reduction in these two solutions were markedly different. The peroxy complex was reduced by more than 10% within one hour whereas the ordinary Cr(VI) complex required eight days to achieve this extent of reduction. Within three days the peroxy complex had been reduced by more than 90%. It was not possible to assign a simple order to the reduction in either case. This does not mean that it could not be first order in Cr(VI) in the organic phase as has been shown for the peroxy complex in an aqueous solution.[207] However, the system examined was fairly complex in that it involved the mixing of two phases and there was no concerted effort to control either the temperature or light.

The spectrophotometric analysis of the peroxychromic acid species extracted from 1M HCl into 0.10M DPPM/CH_2ClCH_2Cl was conducted at 570 nm. The cleanly separated organic phase was placed in the quartz cell and the decrease in absorbance followed for one day. The decrease in absorbance was attributed to a reduction of the 1.9×10^{-4}M Cr(VI) complex. From experiments conducted previously it would be expected that the Cr^{3+} formed would be lost from the organic phase and trapped on the container walls. Assuming that the contribution to the absorbance at 570 nm by the Cr^{3+} reduction product was predictable from the IUPAC reference[210] spectrum ($\varepsilon = 20.8\ M^{-1}\ cm^{-1}$ at 510 nm) an absorption at infinite time, A , was calculated. The plot of $\ln \frac{A - A_\infty}{A_o - A_\infty}$ vs time gave a straight line with a slope of $-6.0 \times 10^{-4}\ min^{-1}$ ($r = 0.997$). This suggests that the reduction reaction for the peroxychlorochromate complex of DPPM in CH_2ClCH_2Cl is first order in Cr(VI) with a rate constant of $6 \times 10^{-4}\ min^{-1}$.

The difference in the rate of reduction of the peroxychromic acid species in the aqueous HCl, mixed organic extract/aqeuous HCl and the organic extract can be qualitatively accounted for if the reduction is assumed to be proton dependent. This decomposition may be formulated as

$$2CrO(O_2)_2Cl^- + 6H^+ \rightleftharpoons 2Cr^{3+} + 3O_2 + 2H_2O + H_2O_2 + Cl^- \quad (4.29)$$

The comparatively rapid reaction in the aqueous system may involve a so-called three-electron oxidation-reduction mechanism similar to that proposed for the reduction of $CrO(O_2)_2$.[207] In the organic extract the protonation of a coordinated peroxo group will be inhibited because nearly all of the available H^+ ions are tied up in the $DPPMH^+$ cation

which is likely to be paired with either Cl^- or $CrO(O_2)_2Cl^-$. In the mixed system there may be access to protons at the interface or there could be a distribution of $DPPMH^+$ $CrO(O_2)_2Cl^-$ to the aqueous phase, even though slight, which could lead to a more rapid reduction than in the cleanly separated organic extract.

The possibility that this extracted peroxychromic acid complex could be used in an analytical procedure was also contemplated. Certainly spectral interference by other metallic species which could be extracted, including Ce(IV) which is the preferred oxidant in such systems, is minimized by the shift of the absorption maximum from 360 nm to 570 nm when peroxide is added to the Cr(VI) extract. Further, it was confirmed that Ce(IV) is rapidly reduced in the acidic solution containing H_2O_2 but the Cr(VI) remained almost quantitatively in the organic phase, subject only to the slow reduction mentioned. Analysis at even lower Cr(VI) concentrations could prove viable by AAS techniques as well. Ichinose et al.[211] have reported such an analysis of the extracted complex in MIBK. However, the distribution ratio was much lower in the MIBK extraction than with the DPPM extraction investigated and there was a significant aluminum interference problem. Further, they stated that the methodology developed was an improvement over other Cr(VI) extractions using MIBK, "limited by the instability of the reagents in acidic solutions", but a reduction in absorbance was noted after 30 minutes. The DPPM extraction could prove to be a superior approach.

This extraction system warrants additional investigation for it could be of value in sorting out some of the physical chemistry involved

in Cr(VI) extractions as well as having an analytical potential. For instance, the extraction process itself must be much quicker than the known rapid reduction of perchromic acid complexes in acidic solutions. It is probable that the practical limitations on reaching distribution equilibrium is not the rate of the extraction process but relates more to the physical mixing of the two phases. This supports the contention that if mixing is efficient there is no advantage in mixing for times even as long as the 5 minutes advocated by Iqbal and Ejaz.[74]

4.2.6 Analytical applications

While this research program was regarded as developmental the findings should contribute not only to an understanding of how to best approach the analysis of chromium at trace levels but also how to accomplish this analysis. Unfortunately, there were no standard reference samples of aqueous solutions available which contained certified amounts of Cr(VI) and Cr(III) at the trace levels of interest. In fact, it is unlikely that such samples will be available since the problems of storage and stability of the oxidation states are not ones which can be overcome easily. It is understandable why real samples are examined directly in such circumstances. Thus, the potential for application of the DPPM extraction system was explored with a few real samples and artificial mixtures.

The initial attempts at analysis involved the use of extracts in 0.10M DPPM/$CHCl_3$. As has been pointed out, the distribution ratio is quite limited when traces of chromium are being examined if Ce(IV) is not present to oxidatively stabilize the Cr(VI) in this system. Therefore, it was decided to first determine total chromium, ie. after

Ce(IV) oxidation, in an aqueous solution by extracting the Cr(VI) and injecting the sample into the graphite tube in an AAS analysis.

Calibration curves were prepared for from 0 to 4 ppb chromium in the aqeuous phase, encompassing the range of concentrations expected for the samples of interest. Different extraction ratios were explored and the volumes of extract injected into the graphite tube were varied from 5 to 20 µL. The calibration curves were linear but all had negative intercepts. In Figure 4.27 such a calibration curve is represented. In this instance the extraction was from a 0.9M HCl solution with the chromium stabilized by 5×10^{-4}M Ce(IV). The extraction ratio was 25/2.* Organic phase samples of 10 µL were injected for analysis. To check that the extraction was consistently effective over the range examined a radiotracer was added to some aqueous solutions. The distribution ratio remained constant at $D = 28 \pm 1$.

Other samples prepared in deionized water yielded similar results. However, the intercept changed with the concentration or brand of HCl used. There was no change with a variation in the Ce(IV) content. It was concluded that the acids contained traces of chromium which became apparent after oxidation and extraction as Cr(VI). In addition to excess Ce(IV) having no detrimental effect on these calibration curves the presence of Fe(III), commonly found with chromium, or Mn(II), present if a permanganate oxidation is chosen, at 3.3 ppm in the aqueous phase caused no difficulties.

Several samples of Lake Ontario water were examined using this approach. These samples, collected by the Water Quality Branch, Inland Waters Directorate (Burlington) in July of 1982 were identified as

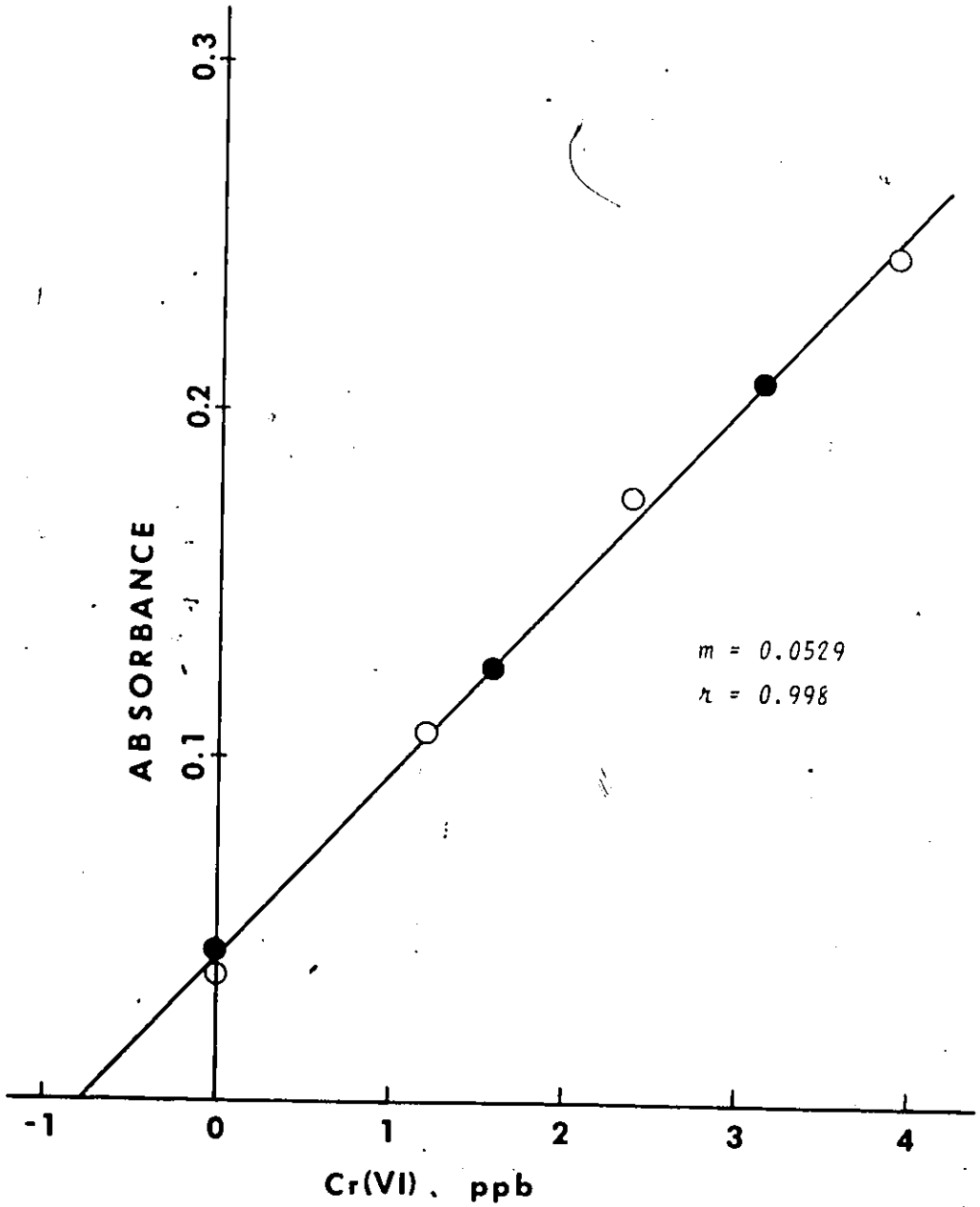
* In all extraction experiments the water sample constituted all but the volume of concentrated HCl (12 M) and Ce(IV), if used, to prepare the aqueous phase. Calculations incorporated the appropriate correction factors.

Figure 4.27

Calibration curve for the extraction of oxidatively stabilized Cr(VI) from an aqueous solution of 0.9 M HCl into 0.10 M DPPM/$CHCl_3$. The extraction ratio used was 25/2. Sample sizes were 10 µL injected into the graphite tube of the AAS spectrometer.

○ ordinary Cr(VI)

● radiotracer present


0.3
0.2
0.1
ABSORBANCE
m = 0.0529
r = 0.998
-1
0
1
2
3
4
Cr(VI), ppb

Station 14, Station 302 and Hamilton Harbour water. The samples had been stabilized by 0.2% HNO_3 so that any chromium present would be as Cr(III). Direct DPPM extractions using $CHCl_3$ as diluent, and later the improved techniques, found no evidence of any Cr(VI). The extraction of these waters by DPPM/$CHCl_3$ after Ce(IV) oxidation was followed by the radiolabelling technique in addition to the analysis by AAS. The distribution ratios varied for the different water samples when extraction was from 0.9M HCl:

Station 14	$D = 8.7 \pm 0.3$
Station 302	$D = 21 \pm 1$
Hamilton Harbour	$D = 6.2 \pm 0.2$

The presence of substances in these waters, including the HNO_3 intentionally added, was sufficient to interfere with the extractions and make the use of any calibration curve impractical.

A standard additions technique proved that it was possible to analyze for total chromium at trace levels in natural waters. However, the chromium content of the HCl would have to be considered. In Figure 4.28 the analysis of Station 302 water is represented. The use of BDH reagent grade HCl at a concentration of 0.60M (5%) in the aqueous phase with $V/\overline{V} = 25/2$ required a correction for this trial (Cr content of BDH HCl = 7.4 ppb). Therefore, in Station 302 water:

$$[Cr]_{analyzed} = 1.38 - 0.37 = 1.01 \text{ ppb}$$

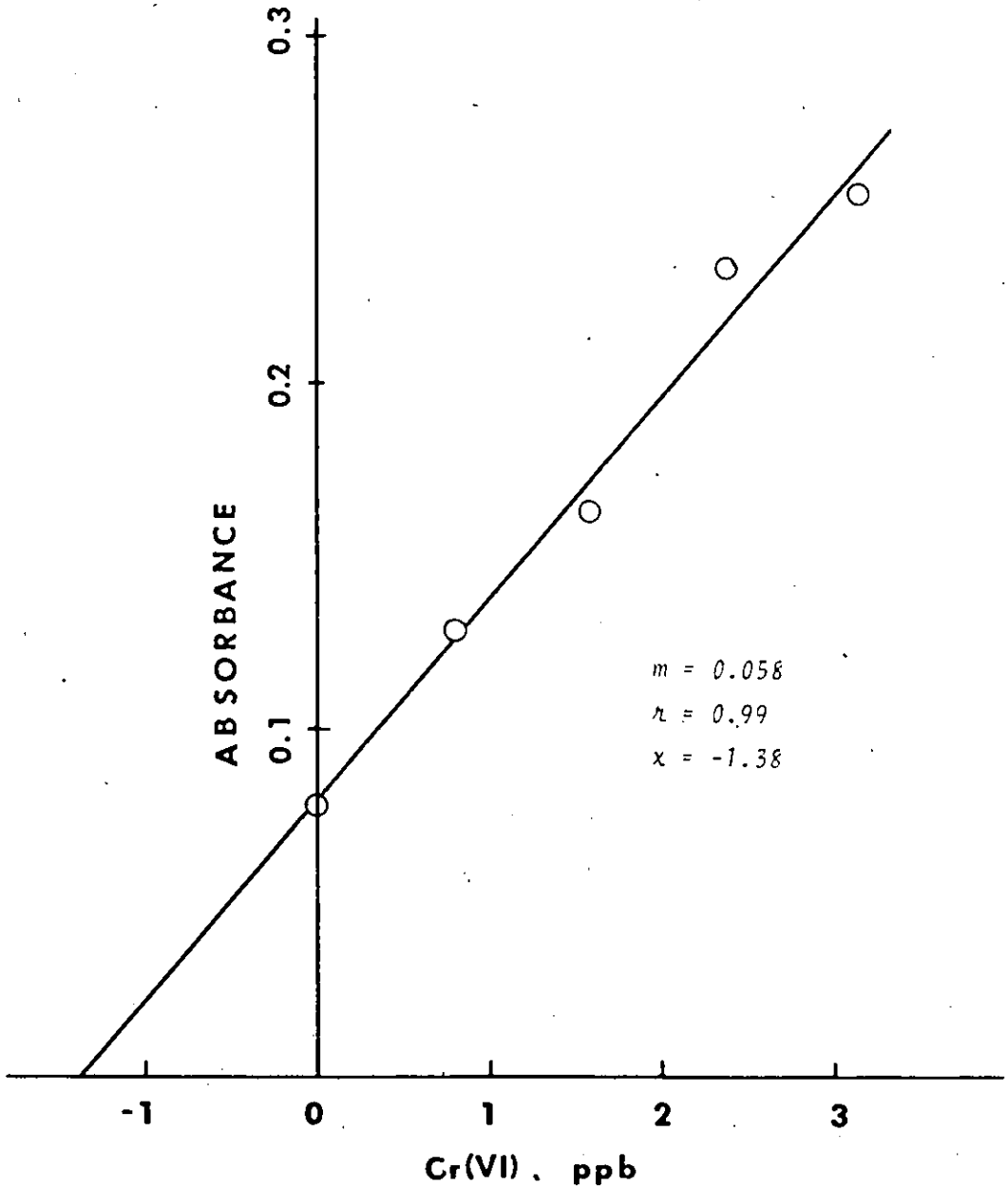
$$[Cr]_{original} = (1/0.95) \times 1.01 = 1.06 \text{ ppb}$$

The chromium content of the Lake Ontario waters were determined using this approach as follows:

Station 14	$Cr = 1.2 \pm 0.2$ ppb

Figure 4.28

The AAS analysis of Cr in Lake Ontario water, Station 302. The technique involved the addition of Cr(VI) standards to a Ce(IV) stabilized solution in 0.6 M HCl. The extraction ratio used was 25/2. Injection volumes were 10 µL.


0.3
0.2
0.1
ABSORBANCE
m = 0.058
r = 0.99
x = -1.38
-1
0
1
2
3
Cr(VI), ppb

Station 302	Cr = 1.1 ± 0.2 ppb
Hamilton Harbour	Cr = 3.0 ± 0.2 ppb

These values were in agreement with results obtained by Chiang and Wan using different methods in the McMaster University Laboratories.[162]

An ocean water sample was also examined to find how effective the extraction procedure would be in eliminating the major matrix problems commonly encountered in analyzing for chromium in such solutions. Again, using the standard additions method, the analysis of the extract by AAS provided a very linear response. By using the extract the bulk of interfering ions had been left in the aqueous phase and the chromium absorption was unhindered. This ocean water had been gathered without filtration as a simple shore sample so as to provide a solution of this type to work with. Nevertheless, the chromium content was estimated by this extraction analysis at a concentration expected for such samples: Cr = 0.4 ± 0.1 ppb.

Although the analysis of chromium in real samples was possible when using the 0.10M DPPM/$CHCl_3$ extraction system the distribution ratio was not ideal in magnitude or reproducibility. The changes with different solutions, and the D values which were sometimes rather low, made the use of a calibration curve suspect. Further speciation of chromium would be difficult under these circumstances. Therefore, the emphasis of the research program was shifted from analysis to a better understanding of the application of extraction to chromium analysis and, most importantly, a means of improving the extraction of Cr(VI) by DPPM.

The success in developing extraction systems for Cr(VI) which are efficient enough to achieve very high distribution ratios in a

variety of solutions with Cr(VI) both stabilized and unstabilized by Ce(IV) has been documented. At this time the number of analyses using the improved technique are limited and there have been no field trials. However, it appears that with a system such as 0.10M DPPM/CH_2ClCH_2Cl the separation/preconcentration process is sufficiently powerful to remove Cr(VI) almost quantitatively from aqueous solutions. According to Corsini, Wan and Chiang[212] the analysis involving such an effective extraction should not require the application of a standard additions method.

A set of calibration curves for the extraction of Cr(VI) from 0.98M HCl by 0.10M DPPM/CH_2ClCH_2Cl is illustrated in Figure 4.29. In each instance 10.0 mL of the aqeuous phase containing the Cr(VI) was extracted by 2.0 mL of the organic phase using a 2 minute contact time. The organic extract was analyzed by injecting a sample and monitoring the signal at 357.9 nm on the atomic absorption spectrometer. The results in Figure 4.29 may be summarized.

Direct extraction

10 µL injection	m = 0.0354	r = 0.995
20 µL injection	m = 0.0719	r = 0.999

Extraction in the presence of 5×10^{-4}M Ce(IV)

10 µL injection	m = 0.0362	r = 0.991
20 µL injection	m = 0.0693	r = 0.994

It can be seen that by doubling the injection volume the signal is increased accordingly. The extractions from both the acid solution itself and in the presence of Ce(IV) give similar slopes, an indication that the enrichment factors are the same in each case. However, there

Figure 4.29

Calibration curves for the extraction of Cr(VI) from 10 mL of a 0.98 M HCl solution prepared in deionized water into 2 mL of 0.10 M DPPM/CH_2ClCH_2Cl. AAS absorbance measurements were recorded at 357.9 nm.

Direct extraction:

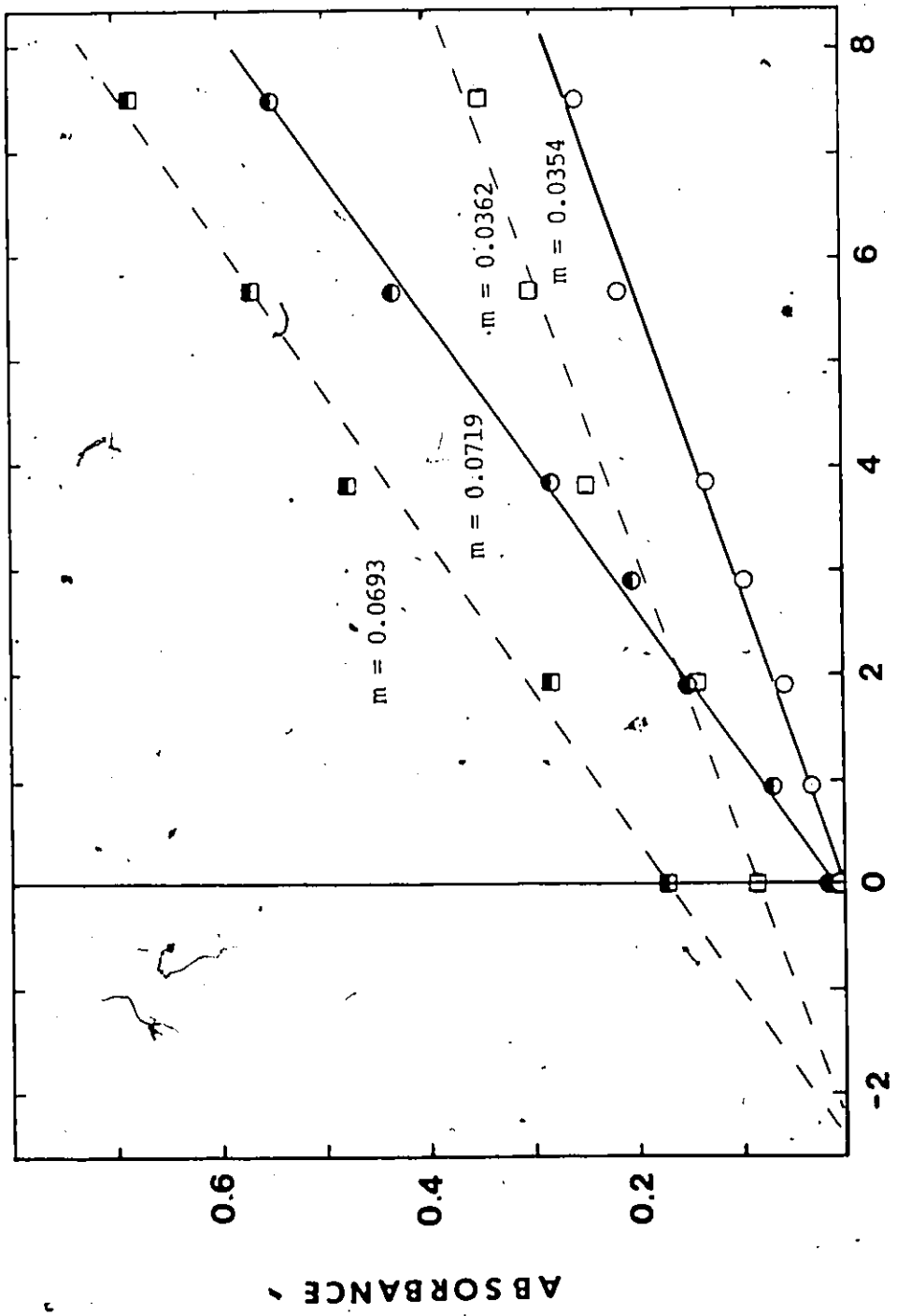
10 µL injections ○

20 µL injections ◓

Extraction in the presence of 5×10^{-4} M Ce(IV):

10 µL injections □

20 µL injections ◓


m = 0.0693
m = 0.0719
m = 0.0362
m = 0.0354
0.6
0.4
0.2
ABSORBANCE
-2
0
2
4
6
8
Cr(VI), ppb

is a nonzero intercept in the presence of Ce(IV), due in all likelihood to the extraction and analysis of the chromium in the acid used.

An analysis of Hamilton city tap water was attempted employing the same extraction conditions. This water at pH 7.5 was not filtered or pre-treated. However, to determine whether or not the calibration curve could be used a labelling experiment was also conducted. $^{51}Cr(VI)$ introduced into the acidified water was extracted. $^{51}Cr(III)$ was added to another sample. After oxidation by Ce(IV) this aqueous solution was extracted. The distribution ratio in each instance was about D = 500. Extraction of any Cr(VI) is likely to be quantitative.

The results for this examination were:

Direct extraction

10 µL injection Absorbance = 0.003 ± 0.002

20 µL injection Absorbance = 0.001 ± 0.002

Extraction in presence of 5×10^{-4}M Ce(IV)

10 µL injection Absorbance = 0.171 ± 0.006

20 µL injection Absorbance = 0.338 ± 0.020

Using the calibration curves it is suggested that there is almost no Cr(VI) in the Hamilton city tap water. However, after oxidation by Ce(IV) the Cr(VI) content in the extract was found to be 2.3 ppb according to the 10 µL injection and 2.4 ppb according to the 20 µL injection. This implies that in the water the chromium must have been as Cr(III) at a concentration of 2.3 ± 0.2 ppb.

Next a spectrophotometric analysis was considered. Since this would have to be with Cr(VI) in the ppm concentration region samples were made up with Cr(VI) from 2 to 9 ppm in 1M HCl aqueous solutions.

0.10M DPPM/CH_2Cl_2 was used as the extractant. In Figure 4.30 the absorbances of the organic extracts at 364 nm in a 1 cm cell are represented for the systems with extraction ratios of 1/1 and 5/3. Both curves are linear and it is apparent that enrichment of the analyte for spectrophotometric analysis is as effective as would have been predicted by the radiotracer experiments. The analysis of aqueous samples with Cr(VI) concentrations over a wide range near 1 ppm, with appropriate choices of extraction ratios, should be possible. However, spectral interferences must be considered. A Ce(IV) oxidation would not be the method of choice if total chromium is to be determined and there may be other elements extracted which cause interference problems not easily overcome (Appendix A and C).

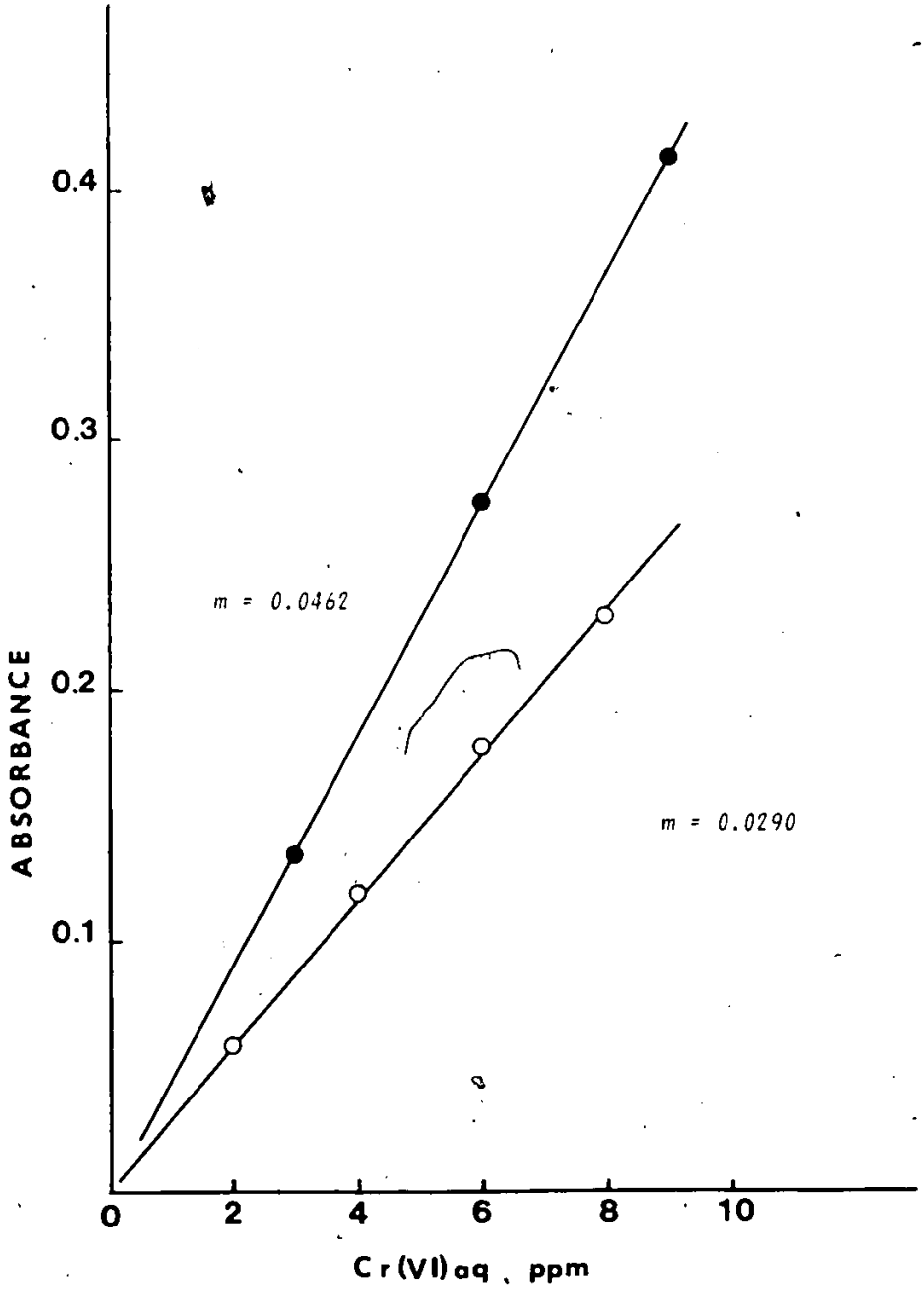
It is the intention that the use of DPPM/diluent extractions be explored further in the analysis of chromium in aqueous solutions. However, it need not be limited to such cases and the potential for use with biological samples should not be overlooked. A simple check, involving the ^{51}Cr(III) radiolabelling of a urine sample, followed by dry ashing and extraction, indicated that it is probable that total chromium could be found in such samples. The labelled Cr(III), probably along with all chromium in such a sample, was converted to Cr(VI) and extracted by the DPPM/diluent.

Figure 4.30

Calibration curve for the spectrophotometric analysis of Cr(VI) in 0.10 M DPPM/CH_2Cl_2 after extraction from an aqueous 1.0 M HCl solution.

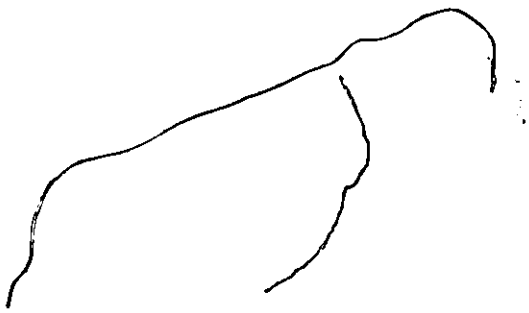
○ Extraction ratio: $V/\overline{V} = 1$

● Extraction ratio: $V/\overline{V} = 5/3$


ABSORBANCE
0.4
0.3
0.2
0.1
m = 0.0462
m = 0.0290
0
2
4
6
8
10
Cr(VI)aq , ppm

There is something fascinating about science.
One gets such wholesale returns of conjecture
out of such trifling investments of fact.

Mark Twain



5. CONCLUSIONS

While as with most research programs there are questions which arise and remain unanswered, the exploration of the reactions of chromium and extraction by DPPM/diluent has led to a better understanding of the problems associated with the trace analysis of chromium. An improved liquid-liquid extraction involving DPPM has been developed which can separate , concentrate and speciate chromium from aqueous solutions. Many of these findings were made possible by the use of a high specific activity ^{51}Cr tracer, others by classical methods such as acid-base titrations and, others still, by spectrophotometric analyses. In general, the various approaches were corroborative.

The preparation of ^{51}Cr by the Sziland-Chalmers reaction on $(NH_4)_2CrO_4$ provided for a high yield but a lower specific activity than was desired. However, while $(NH_4)_2CrO_4$ does not seem to be sufficiently stable under neutron bombardment to permit the preparation of a high specific activity recoil product the separation technique which was developed could prove of general value. In particular, the use of 0.1M DPPM/CH_2ClCH_2Cl to remove the bulk of the Cr(VI), thus leaving the Cr(III) of much higher specific activity in the aqueous phase, should be considered in the examination of other chromates or dichromates under conditions of short irradiation and prompt separation.

When it comes to the handling of aqueous solutions containing trace amounts of chromium there are a number of difficulties which must be recognized. First, the very collection and storage of water containing chromium can be critical if any analysis is to be completed

at a later time in the laboratory. It was shown that Cr(III) is adsorbed on glass and polypropylene. The rate at which this adsorption occurred was inversely proportional to the concentration of Cr^{3+} introduced in the aqueous solution. Reducing the pH or increasing the ionic strength diminished the loss to container walls. Complexes, such as $Cr(C_2O_4)_3^{3-}$, were adsorbed much less than were the inorganic Cr(III) species. Cr(VI) was not adsorbed to nearly the same extent as the Cr(III).

The common practice of acidifying water samples to prevent adsorption losses of this type may be satisfactory if the interest is a simple chromium analysis but not if any speciation is intended. In the presence of acids any Cr(VI) present is subject to reduction. This reduction rate increases as the pH decreases. It too, is subject to a chromium concentration dependence - the reduction rate increases as the Cr(VI) concentration decreases.

If both the total analysis and a speciation of chromium are intended the separation of the different forms would have to be completed at the sampling site. Once separated, if analysis on the spot is not possible, at least the various fractions could be saved as discrete samples for later analysis. This raises the question as to what species are of interest and what is the best speciation approach. Perhaps the identification of Cr(VI) is most important since it is thought to be a hazard in the ecosystem. Nevertheless, there could be interest in the amount of inorganic Cr(III) and Cr(III) complexed with organic reagents since the fate of chromium in the environment is not well understood.[149]

The development of the DPPM/diluent extraction system may have many advantages over the alternative approaches when it comes to both total chromium analysis and speciation of Cr(VI). It has all of the advantages of any such liquid-liquid extraction system, most importantly the ease of application if on site sampling is required. It may be an improvement on the currently favoured extraction procedures involving MIBK.[211] The competing $Fe(OH)_3$ coprocepitation techniques can be used directly only in the determination of inorganic Cr(III)[94] and, generally, Cr(VI) and organic complexes of Cr(III) are not differentiated after a reduction procedure. Ion-exchange procedures have been questioned,[54,94] and in this program it has been shown that speciation by an ion-exchange approach is suspect. All Cr(III) need not be cationic an all anionic chromium need not be Cr(VI). It is very difficult to discriminate between anionic Cr(VI) and anionic species such as $Cr(C_2O_4)_3^{3-}$.

With a careful selection of the DPPM/diluent solution and preparation of the aqeuous phase it is possible to extract Cr(VI) almost quantitatively. Addition of a Ce(IV) oxidant to the system permits the extraction of Cr(III), once oxidized, so that a total chromium analysis is possible. However, the choice of diluents and the type and concentration of acid added to the aqueous phase is critical.

In the extraction using DPPM the diluent plays a very important role. The best extractions of Cr(VI) involved the hydrogen bonding diluents $CHCl_3$, CH_2Cl_2 and CH_2ClCH_2Cl. Within this group the distribution ratio for Cr(VI) was found to increase with an increase in the dielectric constant. Therefore, the extraction system that should

best meet the objective of removing Cr(VI) from an aqueous solution would be one employing 0.10M DPPM/CH_2ClCH_2Cl. This diluent also has other advantages. It is the least soluble of the three diluents and separates cleanly from the aqueous phase under a gravitational field alone. It is the least volatile, and thus easier to work with if being injected into the graphite tube in an AAS analysis or being placed in an absorption cell for a spectrophotometric analysis.

Cr(VI) is extracted best from HCl solutions, and these extractions were examined in some detail. It can be extracted to a lesser extent from H_2SO_4 and HBr but not well from $HClO_4$ and HNO_3. However, the extraction of the acids themselves is not in this order. Using 0.10M DPPM/diluent systems it was shown by two phase titrations that the order of acid extraction is

$$HClO_4 > HNO_3 > HBr > HCl > H_2SO_4 , H_3PO_4$$

This order is a reflection of the aquaphobic nature of the respective anions when paired with the protonated DPPM. The fact that DPPM is completely protonated in the organic phase by 1M $HClO_4$ led to the development of a technique which can be used to find the amount of DPPM in the aqeuous phase in an extraction system.

In the extraction from HCl solutions there is an acid concentration dependence. The pattern is the same for each diluent, with a gradual increase in the distribution ratio as the HCl concentration increases, an optimum value near 1M in HCl, and a decrease thereafter as the acid concentration increases. While the phenomenon is similar, the actual values of the distribution ratios vary with the

diluent. As mentioned, the extent of extraction parallels the dielectric constant so that the maximum values of D are respectively:

$$D(CH_2ClCH_2Cl) \approx 700, \qquad D(CH_2Cl_2) \approx 300$$

$$D(CHCl_3) \approx 30$$

It is seldom that one sees more than a rudimentary explanation for the extractions of this type in the chemical literature. Despite the recognition that it would be difficult to assign activities to the various components and there would be problems in choosing the best values for the equilibrium constants involving Cr(VI), some of which have very divergent literature values or are not available at all, an attempt to provide a model for this extraction was undertaken.

In acid solutions alone, or with Cr(VI) at trace concentrations, the distribution of the complexes of DPPM that arises when the aqeuous acidic solution is mixed with the organic phase containing initially all of the DPPM, is determined by the concentration of the acid. While fairly detailed, in essence the model accounts for the observed distribution of DPPM complexes in the two phases. It suggests that the amount of $DPPMH^+$ is near a maximum in 1M HCl solutions. Further, the distribution of the DPPM complexes depends upon the diluent used. The order of HCl extraction would be as found experimentally:

$CHCl_3 > CH_2Cl_2 > CH_2ClCH_2Cl$.

If present, Cr(VI) must compete with the anions of the acid for the pairing sites on $DPPMH^+$. The availability of the $DPPMH^+$ depends on the diluent and the acid concentration and, of course, on the initial concentration of DPPM introduced in the organic phase. Moreover, according to the model the optimization of the distribution ratio could

be best accounted for if not only the $DPPMH^+$ was optimized near 1M HCl but also the species extracted was CrO_3Cl^-. The model also suggests that the distribution ratio should be independent of the Cr(VI) concentration, at least up to a concentration at which large activity changes become important. Experimental evidence supports this contention.

The Cr(VI) species extracted from HCl solutions into DPPM/diluent must be primarily CrO_3Cl^-. Not only is this consistent with the proposed extraction model but spectral evidence supports this assignment. In the UV-visible spectrum the fine structure of the charge transfer absorption band is that expected for CrO_3Cl^-.[190,192,193] The FT-IR evidence irrefutably indicates that there is an absorbance which has been assigned to the Cr - Cl vibration.[199,200] Despite the claim by Iqbal and Ejaz[74] that the $HCrO_4^-$ complex is the species extracted at low Cr(VI) concentrations, this complex alone could not account for the evidence cited. However, while the very existence of such a species as $HCrO_4^-$ was questioned by Michel and Machiroux[202] in 1983, this research program can only suggest that in the extraction by DPPM/diluent from aqeuous HCl solutions it must be of minor significance.

The extraction from other acids is not as favorable as from HCl. Part of this may be related to the availability of the extractant for ion-pair formation with the Cr(VI). Either it is not in the correct form or it is already tightly bound to the anions of the acid. However, much of the problem must be due to the form of Cr(VI) present in the system. If a Cl^- salt is added there is a dramatic increase in the extractability of the Cr(VI). This suggests that in the presence of Cl^-

there is the formation of a species, such as CrO_3Cl^-, which can be extracted much more readily than other Cr(VI) complexes. Even the species in H_2SO_4, while extracted to some extent, forms a less hydrophobic ion-pair with $DPPMH^+$ than does CrO_3Cl^-.

The usefulness of DPPM in the extraction of Cr(VI) has been confirmed. From HCl solutions it is possible to concentrate the Cr(VI) and in so doing make the analysis easier when traces are involved. The extraction also separates the Cr(VI) from a number of interfering species and provides for a uniform matrix. This can be of considerable value when chromium is to be determined in the complex solutions sometimes encountered in industrial effluents or ocean waters. While the chromium content in the extract can be determined directly it is also possible to back extract the Cr(VI) if an aqueous phase analysis is preferred.

Not only does the extraction provide for the separation of Cr(VI) from most other metallic species but it also permits the separation of Cr(VI) from Cr(III). The separation factor for Cr(VI)/Cr(III) is large. Therefore, while the Cr(VI) can be extracted and concentrated in the organic phase the Cr(III) remains in the aqueous solution. Both inorganic Cr(III) and anionic complexes of Cr(III), such as $Cr(C_2O_4)_3^{3-}$, can be distinguished from Cr(VI). However, if the total chromium content of a sample is of interest, oxidation by Ce(IV) is effective, even at room temperature, and the oxidized chromium can be extracted.

For the final analysis of chromium both AAS and spectrophotometric methods are suitable. ETA-AAS analysis of the

extract is recommended when the chromium content is in the low ppb concentration range, spectrophotometric analysis is possible with ppm chromium samples.

While the overall approach has been successful with laboratory samples, the application to real systems is limited. However, the concern expressed about carcinogenic chromium in the public water supplies derived from Lake Ontario[1] does seem to be unjustified and somewhat alarmist. In the analysis employing the extraction technique none of the water samples from Lake Ontario had a chromium content even near to the maximum acceptable limits according to the Guidelines for Canadian Drinking Water Quality.[7] Further, in the analysis of Hamilton city tap water, the chromium in the distributed water appeared to be in the safe Cr(III) oxidation state. Perhaps if an improved sampling/analytical technique, such as that developed with 0.1M DPPM/CH_2ClCH_2Cl, can be applied so that speciation as well as the total chromium content in environmental samples can be ascertained there will be a better understanding of the role of chromium in the environment.

If you are out to describe the truth, leave the elegance to the tailor.

Albert Einstein

APPENDIX A

Extraction Problems

The intent of this appendix is to illustrate the use of the enrichment factor (F) parameter described in Section 2.2. This is demonstrated by posing three problems, all related closely to the actual research.

1. Problem. A sample of ocean water is to be analyzed for Cr. With the AAS instrument available it is difficult to obtain reliable results in such a matrix at the expected Cr concentration near 0.3 ppb. It is desirable to work in a simple matrix in which Cr is near a concentration of 6 ppb. While solvent extraction may provide for the desired separation of Cr, the system must be examined to determine whether or not it is possible to achieve sufficient enrichment in a single extraction.

   a) Can the system described by Iqbal and Ejaz[74], using 0.100M DPPM/$CHCl_3$, achieve the desired enrichment?

   b) Employing the improved methodology with 0.100M DPPM/CH_2ClCH_2Cl what is the most reasonable extraction ratio which could be used to achieve the desired separation and enrichment? What proportion of the Cr is extracted into the organic phase?

Answer

a) The desired objective is F = 6 ppb/0.3 ppb = 20. Using equation (2.23) with the value of D = 3 reported[74], it can be shown that at any extraction ratio x,

$$F = \left(\frac{D}{D + V/\overline{V}}\right) y/\overline{V} = \left(\frac{3}{3 + x}\right) x < 3$$

The desired enrichment is not possible.

b) Using the improved technique with D = 800, it can be shown that

$$F = 20 = \left(\frac{800}{800 + x}\right) x \quad , \quad x = 20.5$$

The most reasonable extraction ratio $V/\bar{V} = x = 20.5$.

Rearranging equation (2.22)

$$\%E = (100\ F)(\bar{V}/V) = (100)(20)(1/20.5) = 97.5\%$$

When calculating the concentration of Cr in the ocean water it must be remembered that only 97.5% is extracted into the organic phase.

2. Problem: Cr(VI) and Cd(II) are to be separated from an aqueous solution in which they are both initially at a similar concentration, say 1 ppm. It has been determined that from a solution acidifed to 0.8M HCl the distribution ratios for 0.10M DPPM in chloroform and 1,2-dichloroethane are:

$D_{Cr}(CHCl_3) = 30$ $\quad$ $D_{Cr}(CH_2ClCH_2Cl) = 800$

$D_{Cd}(CHCl_3) = 0.24$ $\quad$ $D_{Cd}(CH_2ClCH_2Cl) = 6.5$ $\quad$ (Appendix C)

ie. $\alpha_{Cr,Cd} = 30/0.24 = 125$ and $800/6.5 = 123$ respectively.

a) Which diluent should be used when equal volumes of the aqueous and organic solutions are mixed if the ratio of extracted Cr(VI) to Cd(II) is to be greatest in the organic phase?

b) If $V/\bar{V} = 20$ what is the ratio of Cr(VI) to Cd(II) in the organic phase with each of the diluents?

Answer

a) Since the separation factor α is virtually identical for each extraction system it cannot determine the effectiveness of the separation.

However, the concentrations of Cr(VI) and Cd(II) in each organic diluent can be determined easily since they must equal F multiplied by the original aqueous concentrations.

In $CHCl_3$:

$[\overline{Cr}]$ = (30/30+1)(1)(1) = 0.968 ppm, $[\overline{Cd}]$ = (0.24/0.24+1)(1)(1) = 0.194 ppm

Ratio = $[\overline{Cr}]/[\overline{Cd}]$ = 0.968/0.194 = 5.0

In CH_2ClCH_2Cl:

$[\overline{Cr}]$ = (800/800+1)(1)(1) = 0.999 ppm, $[\overline{Cd}]$ = (6.5/6.5+1)(1)(1) = 0.867 ppm

Ratio = $[\overline{Cr}]/[\overline{Cd}]$ = 0.999/0.867 = 1.15

ie. chloroform meets the criteria best for separation.

b) In $CHCl_3$:

$[\overline{Cr}]$ = (30/30+20)(20)(1) = 12.0 ppm, $[\overline{Cd}]$ = (0.24/0.24+20)(20)(1) = 0.24 ppm

Ratio = $[\overline{Cr}]/[\overline{Cd}]$ = 12.0/0.24 = 50 Note: [Cd]/[Cr] = 125/50 = 2.5

In CH_2ClCH_2Cl:

$[\overline{Cr}]$ = (800/800+20)(20)(1) = 19.5 ppm $[\overline{Cd}]$ = (6.5/6.5+20)(20)(1) = 4.9 ppm

Ratio = $[\overline{Cr}]/[\overline{Cd}]$ = 19.5/4.9 = 4.0 Note: [Cd]/[Cr] = 123/4.0 = 31

3. Problem: A 0.6M HCl solution containing Cr(VI), expected to be at a concentration near 0.2 ppm (4×10^{-6}M), and Fe(III), at a concentration of about 100 ppm (2×10^{-3}M), is to be analyzed for chromium spectrophotometrically in a 1 cm absorption cell. Since the absorbance due to Fe(III) in such an aqueous solution is substantial it would not be possible to determine the concentration of Cr(VI) even at a much higher concentration than 0.2 ppm.

a) Will a single extraction using 0.100 M DPPM/CH_2Cl_2 permit successful analysis by an examination of the organic phase?

b) Would a second (multi-stage) extraction of the solution be advantageous?

c) Would a single scrubbing after the batch extraction permit an improved analysis?

Answer:

a) For the extraction using 0.10M DPPM/CH_2Cl_2 from 0.6 M HCl solution it has been determined that $D_{Cr(VI)} = 350$ and $D_{Fe(III)} = 0.02$ (Appendix C). The absorbance maximum for Cr(VI) in the organic phase is shifted to λ = 364 nm with a molar absorptivity of 1600 $M^{-1}cm^{-1}$. From this work it has been shown that while the absorption maximum for Fe(III) in 0.6M HCl is at λ = 335 nm there is still a substantial absorption at λ = 364 nm. The estimated molar absorptivity of 815 M^{-1} cm^{-1} at λ = 364 nm would be in substantial agreement with the investigation by Desesa and Rogers[213]. To be reliable the absorptivity of the Cr(VI) should be at least 0.1 absorbance unit and the absorptivity of the Fe(III) less than 1% of this value.

From Beer's Law at λ = 364 nm:

$[Cr(VI)] = A/\varepsilon L = 0.1/(1600)(1) = 6 \times 10^{-5}$ M

$[Fe(III)] = A/\varepsilon L = 0.001/(815)(1) = 1 \times 10^{-6}$ M

Utilizing the F parameter it is estimated that the enrichment of Cr(VI) should be at least.

$F = 6 \times 10^{-5}/4 \times 10^{-6} = 15$

Using an extraction ratio ($V/\bar{V}$) of 20 the concentration of Cr(VI) and Fe(III) in the organic phase can be determined by using the F parameter and the approximate concentration of the metalic species in the original aqueous solution.

$[\overline{Cr}] = (350/350+20)(20)(4 \times 10^{-6}M) = 7.57 \times 10^{-5}M$

$[\overline{Fe}] = (0.02/0.02+20)(20)(2 \times 10^{-3}M) = 4.00 \times 10^{-5}M$

The Cr(VI) is now in a reasonable concentration range for analysis but the Fe(III) present is still at a sufficient concentration to cause problems. A successful analysis is in doubt.

b) Employing equation (2.22) it can be shown that 94.6% of the Cr(VI) has been removed from the aqueous phase but only 0.1% of the Fe(III) is extracted. A second extraction of the aqueous phase would be of no value. Adding the second organic extracted portion to the first would only make things worse - more Fe(III) but little Cr(VI) would be contributed; ie. $[\overline{Fe(III)}]$ = similar, $[\overline{Cr(VI)}]$ = lower.

c) Scrubbing the extracted organic solution by equilibrating it with an equal volume of 0.6M HCl prepared in deionized water would lead to the following situation in the separated organic phase:

$[\overline{Cr}] = (350/350+1)(1)(7.57 \times 10^{-5}M) = 7.55 \times 10^{-5}M$

$[\overline{Fe}] = (0.02/0.02+1)(1)(4.00 \times 10^{-5}M) = 0.08 \times 10^{-5}M$

The absorbance due to Cr(VI) would be nearly unchanged at about 0.12 absorbance units but for the Fe(III) it would be about 0.0006 absorbance units. A single scrubbing has reduced the interference by Fe(III) sufficiently that there can be some confidence that an analysis of Cr(VI) will be successful.

APPENDIX B

Reactions of Chromium

Oxidizing - reducing agents

The oxidation - reduction behavior of chromium at trace concentrations in the presence of several reagents was examined.

In acid solutions H_2O_2 was most effective in reducing high specific activity $^{51}Cr(VI)$ to $^{51}Cr(III)$. According to the standard reduction potentials[186] this is a favorable process:

$$HCrO_4^- + 7H^+ + 3e^- \rightleftharpoons Cr^{3+} + 4H_2O \qquad E^\circ = 1.195V \qquad (B.1)$$

$$O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O_2 \qquad E^\circ = 0.682V \qquad (B.2)$$

However, in a basic solution H_2O_2 was used to oxidize Cr(III) to Cr(VI).

$$H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O \qquad E^\circ = 1.776V \qquad (B.3)$$

While not as convenient as a Ce(IV) oxidation, and care had to be taken to remove excess H_2O_2 by boiling the solution, this oxidation process was used when an analysis by spectrophotometric methods was undertaken.

Ammonium peroxodisulfate, the source of $S_2O_8^{2-}$, is a potent oxidizing agent in acid solutions ($E^\circ = 2.0V$)[186] and is commonly used to convert Cr(III) to Cr(VI).[169] Although generally used with an Ag^+ catalyst, the excess reagent is readily destroyed by boiling and the procedure should introduce no substance that can interfere with the analysis of Cr(VI) by AAS or spectrophotometric means. Unfortunately, under no circumstance investigated was the oxidation quantitative. Chuecas and Riley[55] and Blundy[214] have also reported that such oxidations are not satisfactory with µg amounts of chromium.

Potassium permanganate is a powerful oxidant and in an acidic solution forms Mn^{2+} according to the reaction:[186]

$$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O \qquad E^\circ = 1.491V \qquad (B.4)$$

However, the oxidation of Cr(III) by MnO_4^- did not proceed satisfactorily at room temperature and heating was required. To prepare the $^{51}Cr(VI)$, excess $KMnO_4$ was added to the acidic $^{51}Cr(III)$ tracer solution and it was heated to near boiling. Although some MnO_2 tended to form, as evidenced by the slight brown coloration remaining after the disappearance of the purple MnO_4^-, it was possible to use sodium azide to prevent accumulation of this undesired product. With care the oxidation was satisfactory albeit somewhat tedious, although it has been dismissed as being not effective or reproducible by Bryson and Goodall[36] and Blundy.[214]

Another powerful reagent used in the oxidation of Cr(III) at trace levels is the Ce(IV) ion.[49,72,73,165,214] The standard reduction potential for the reaction

$$Ce^{4+} + e^- \rightleftharpoons Ce^{3+} \qquad (B.5)$$

tends to vary with the acid medium employed. Most commonly the value is listed with sulfuric acid since Ce(IV) is remarkably stable in this acid; $E^\circ = 1.44V$ in $1N\ H_2SO_4$.[169]

Despite the fact that there is a slow oxidation of chloride ion by Ce(IV) the goal of being able to achieve complete oxidation of Cr(III) in HCl solutions dictated that an attempt be made to stabilize Cr(VI) in such systems. One reason for this is that many natural solutions have a high chloride content. More importantly, the DPPM extraction is most effective from HCl solutions.

It was found that in the presence of excess Ce(IV) the oxidation of $^{51}Cr(III)$ was complete well within 30 minutes, even at room temperature, and the chromium remained in the higher oxidation state for a considerable period of time, depending upon the amount of Ce(IV) used. A number of examinations of this production of Cr(VI) and its stability

were conducted but a single example can demonstrate the process.

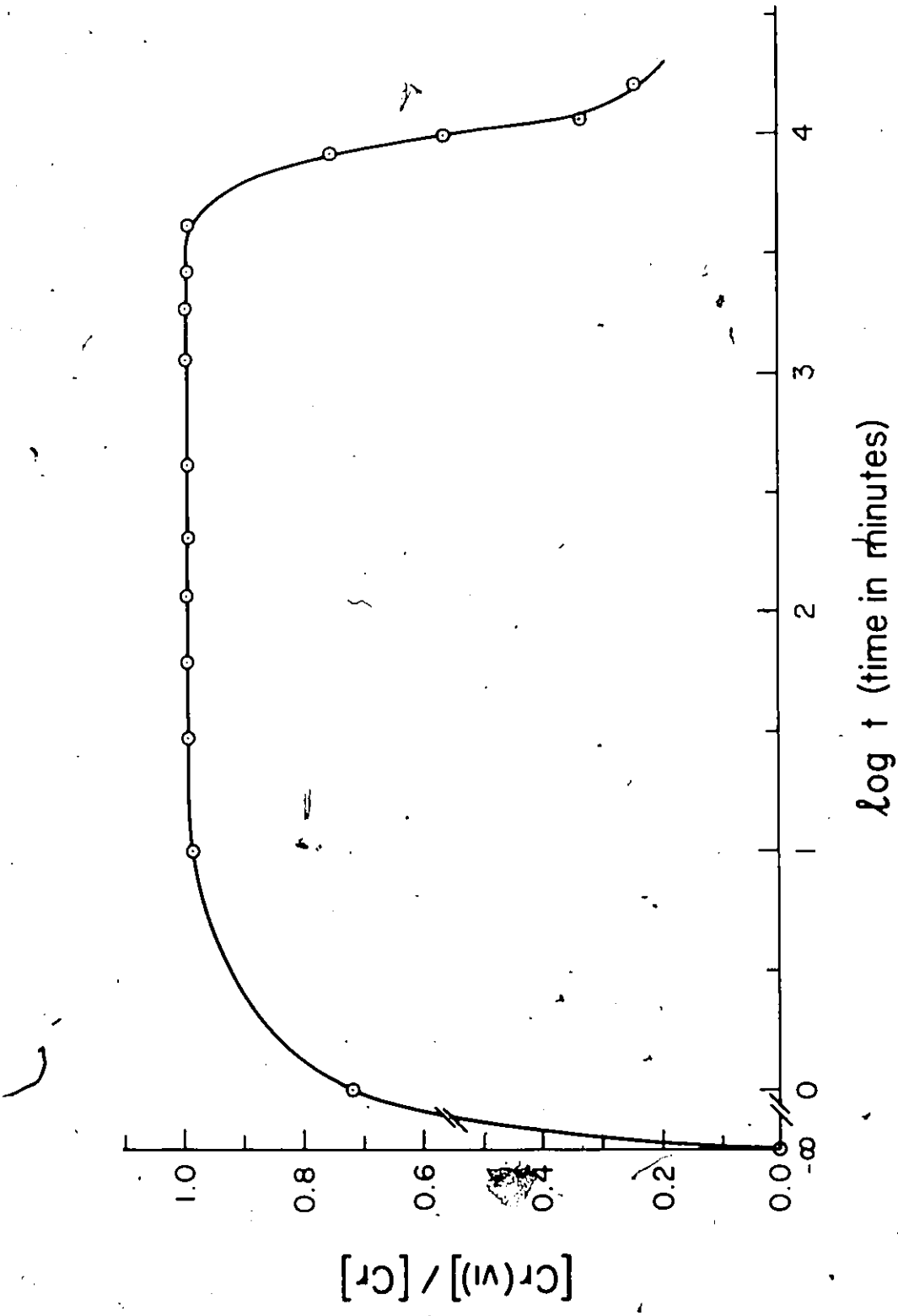
Figure B.1 represents the results for a study that was conducted for 11 days. To this system containing $^{51}Cr(III)$ at 10 ppb in 1.0M HCl was added Ce(IV) to a concentration of 2.5×10^{-3}M. The activity in each oxidation state of the chromium was assessed at various times after mixing. Since the first analysis was at 1 minute after adding the Ce(IV) and the last after 264 hours a logarithmic scale best represents the time. Rather than representing each oxidation state only the ratio of $^{51}Cr(VI)$ to the total ^{51}Cr is shown.

The indication that the oxidation of Cr(III) is reasonably rapid is confirmed by other trials as well. Generally, less than 1% of the chromium, initially introduced as $^{51}Cr(III)$ in the HCl solution, will pass through an anion-exchange resin after contact with Ce(IV) for 10 minutes at room temperature. Extraction procedures corroborated the evidence that Cr(VI) was formed quite rapidly. In the presence of 2.5×10^{-3}M Ce(IV) the Cr(VI) is stable for about 3 days. Thereafter, there is a gradual reduction, and by 6 days only about 75% remains in the higher oxidation state.

A detailed report on such an oxidation of Cr(III) at trace levels by Ce(IV) is not available although the kinetics and mechanism of the oxidation process at mM concentrations in H_2SO_4 has been reported by Tong and King.[215] However, the oxidation is much more rapid in $HClO_4$,[215] is said to be complete within 2 minutes in HNO_3[53] and it is probable that it would be faster in HCl as well. As long as the Ce(IV) remains in solution the Cr(VI) remains oxidized. However, when the Ce(IV) is eventually reduced, as expected in the HCl solution[169], the Cr(VI) experiences reduction.

Figure 8.1

The determination of the rate of oxidation of 10 ppb Cr(III) and the stability of the anionic Cr(VI) in 1 M HCl in the presence of excess Ce(IV).


[Cr(VI)] / [Cr]
1.0
0.8
0.6
0.4
0.2
0.0
-∞
0
1
2
3
4
Log t (time in minutes)

The oxidation of $^{51}Cr(III)$ introduced as a label in natural waters was examined in a similar manner. With the Lake Ontario waters and the ocean water sample there was satisfactory oxidation in the presence of 1×10^{-3}M Ce(IV). However, the Cr(VI) produced in these cases tended to be stable for a shorter period of time than with the deionized water. This probably reflects the fact that a considerable portion of the Ce(IV) is consumed in the oxidation of substances in these waters besides the Cr(III). A more intensive examination of the contents of the natural waters is warranted but was beyond the scope of this research program. More Ce(IV) could be added if the reduction of the Cr(VI) became apparent but, in general, if the separation procedure was initiated at 30 minutes after the primary oxidation the removal of Cr(VI) from such solutions was satisfactory (Section 4.2).

Reduction phenomena

The reduction of Cr(VI) at trace levels, when no reducing agent had been intentionally added, was examined in both solution and on ion-exchange resins. There was no reduction of the high specific activity $^{51}Cr(VI)$ at pH > 6.5 so that this material could be used to prepare 20 ppb Cr(VI) samples at various pH values, adjusted with HCl or acetate buffers.

In a 0.01M acetate buffer reduction was slow at pH 5.4, about 5% in one day. As the pH was lowered the rate of reduction increased (Table B.1). Reduction at lower pH values would be expected (Figure 1.1), indeed in 1M HCl reduction was complete well within 1 hour, but when dealing with traces of $^{51}Cr(VI)$ it had not been predicted that reduction would be a concern above pH 2.

Table B.1

The rate of reduction of Cr(VI) in acidic solutions at trace levels of 20 ppb Cr(VI). The proportion of Cr(VI) remaining in solution at different pH values is reported for various times after mixing.

time (hours)	pH 4.1 (acetate) 25 ± 1°C	pH 4.1 (acetate) 37 ± 1°C	pH 4.1 (acetate) 60 ± 1°C	pH 3.0 (Cl^-) 25 ± 1°C	pH 2.6 (Cl^-) 25 ± 1°C
0.08				0.993	
0.5				0.986	0.952
1.0	0.972		0.968	0.970	0.906
2.5		0.982		0.94	
9.0	0.961		0.587		
10.0		0.82			
20.0			0.18	0.86	0.72
21.5	0.93	0.66			
24.0					0.70
26.0	0.91			0.80	
33.0		0.52	0.15		
48.0				0.64	0.52
72.0				0.55	0.31

In the trial at pH 4.1, Table B.1, as well as confirmatory trials at other pH values, it is apparent that there is a marked increase in the rate of reduction of Cr(VI) with an increase in temperature. However, data sufficiently reliable to report an activation energy for the reaction is not yet available.

Also observed, as suggested by Lukkari[97], was the striking increase in the rate of reduction of Cr(VI) in solution as the initial concentration was lowered. With solutions from pH 2.1 to 4.1 the concentration of $^{51}Cr(VI)$ was varied and the proportion of the activity in each oxidation state determined at intervals of time after mixing. As an example, when compared to the pH 4.1 sample of 20 ppb Cr(VI) at 25°C, where reduction was about 8% in one day (Table B.1), a sample of 200 ppb Cr(VI) was reduced only about one third as fast and a sample of 1 ppm Cr(VI) had no measurable reduction in one day. Even at pH 2.1 the reduction of 100 ppb Cr(VI) in one day was only 15%, ie. about ½ that of a 20 ppb Cr(VI) sample at a higher pH 2.6 (Table B.1).

Is reduction of Cr(VI) on anion-exchange resins appreciably different from that in solution? To examine this effect various amounts of Cr(VI), labelled with the high specific activity $^{51}CrO_4^{2-}$, were loaded in to columns containing AG1-X4 resin in the chloride or acetate form. The effluent from the various trials was collected, counted and speciated. In some cases the activity changes in the columns were followed by counting the columns at various positions.

Initial investigations were conducted by loading less than 1 ng of Cr(VI) on to the resins in the Cl^- form and then batch washing with water and with 0.1M HCl over a three day period. The water removed

less than 1% of the activity while the 0.1M HCl removed an appreciable portion, all as Cr(III). It was noticed that when using a standard 2.1 mL of 0.1M HCl the amount of activity removed depended primarily upon the length of time between elutions - the longer the time Cr(VI) on the resin was left in contact with acid solution the greater the reduction and removal of the activity in the subsequent wash.

Further experiments indicated that beyond 1 mL the volume of solution used to wash the column and remove activity made little difference, except in those cases with very acidic solutions in which reduction was rapid. The column effluent contained Cr(III) since there was little displacement of Cr(VI) with the 0.1M reagents used; with 0.5M KCl solutions some displacement was apparent.

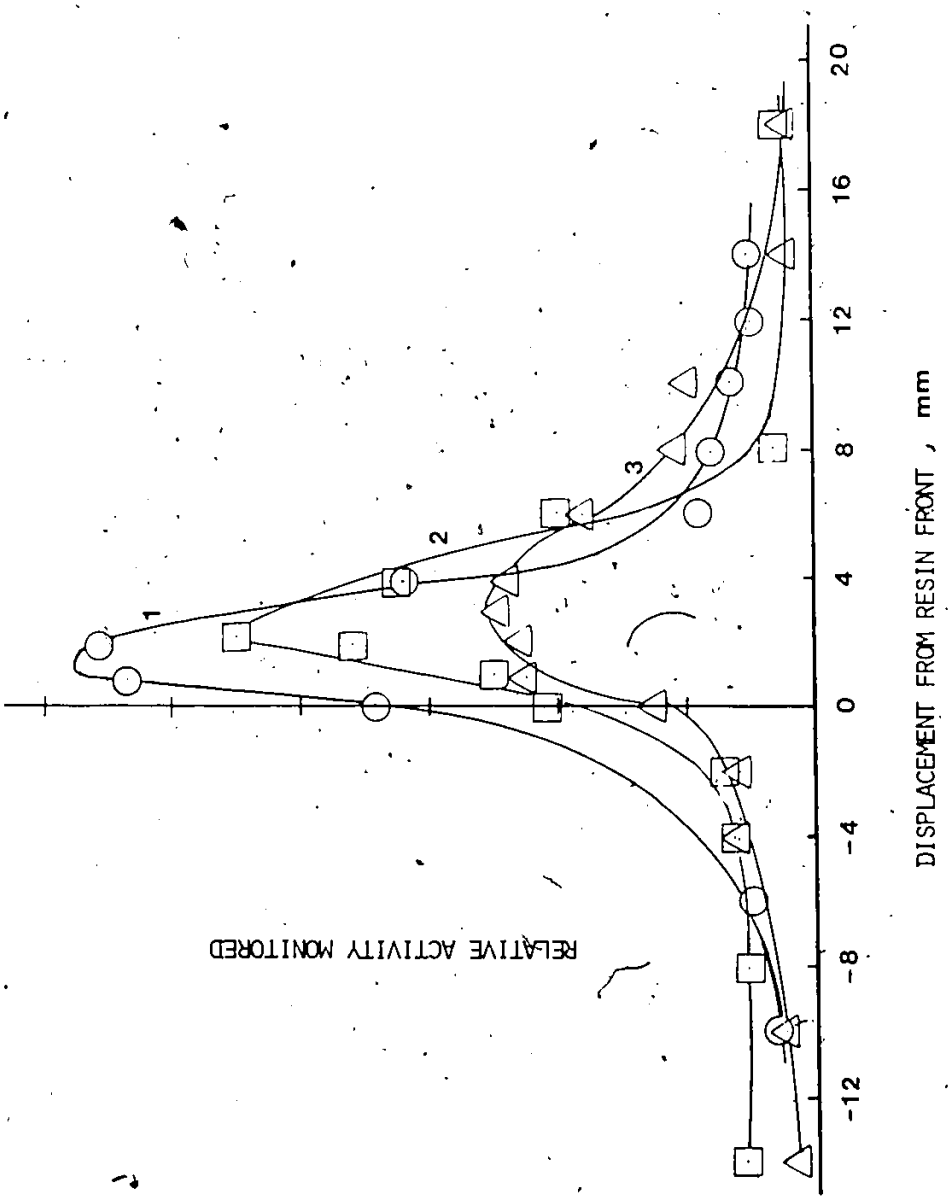
Since 0.1M acetic acid/sodium acetate solutions permitted better control of pH a number of such solutions containing a $^{51}Cr(VI)$ label were placed in AG1-X4(acetate) anion-exchange columns and washed with the same solution containing no label. Using 0.1M acetic acid, pH 2.9, there was a slow loss of activity from the column. As expected from the solution studies, there was reduction, but not as rapid as with 0.1M HCl. With 0.1M sodium acetate no activity was removed. Using buffer solutions of various pH values it was confirmed that, just as with the solution experiments, the rate of reduction increased as the pH decreased.

The activity profiles of ^{51}Cr on the mini-columns of resin demonstrate conclusively that the reduction occurs in the columns and not in the eluent subsequent to separation. Figure B.2 represents such an examination where the removal of activity by an acetate buffer solution

Figure B.2

Column resin activity profile for 4 ng of labelled Cr(VI) after washing with an acetate buffer solution of pH 4.8.

1. Initial column activity profile ○
2. Column activity profile after 3 hours □
3. Column activity profile after 21 hours △


RELATIVE ACTIVITY MONITORED
DISPLACEMENT FROM RESIN FRONT , mm
20
16
12
8
4
0
-4
-8
-12
1
2
3

of pH 4.8 was monitored. Column resin activity profiles for other solutions are almost identical in shape. It can be seen that the activity of the labelled 4 ng of Cr(VI) is located initially within 2 mm of the resin surface. Of course, since the slit has a width of 1 mm there is activity detected adjacent to the most active areas and there is also a general activity detected through the lead block. Subsequent additions of the buffer solution spreads the activity slightly further into the column. However, the Cr(VI) is not displaced appreciably while the Cr(III) reduction product is almost completely removed. Part of the spreading of the Cr(VI) activity may be due to disturbance of the resin particles. In the trial illustrated, the first curve represents the distribution of the activity of about 28000 ± 170 c/min, measured in the well counter before placement on the column, after it has been washed with 6 mL of the buffer solution. Curve two is after 3 hours. The activity removed by 2.1 mL of solution was 3680 ± 60 c/min, all as Cr(III). Curve three, after 21 hours, represents a loss of 8460 ± 90 c/min, again all as Cr(III).

The amount of Cr(VI) placed on the resin is important in that the proportion of the material reduced in a given time is much greater with the smaller sample. To illustrate this two columns were prepared identically but for the amount of Cr(VI) and were washed with 2.1 mL of 0.1M HCl solution at the same time intervals. The proportion of the activity removed, all as Cr(III), was found to be different when 40 ng were used instead of 10 ng.

time (hours)	0	1	2.5	8.3	25.6
reduction for 10 ng	0.005	0.034	0.082	0.163	0.268
reduction for 40 ng	0.004	0.020	0.047	0.089	0.163

The reduction of Cr(VI) at trace levels on anion-exchange resins does not seem appreciably different from that in solution. The longer the contact with the acidic solution the greater the reduction. The proportion of the sample reduced in a given time is greater when the amount of Cr(VI) is smaller. Therefore, recognition of this reduction problem becomes most important when very low levels of Cr(VI) are being used.

Cr(III) oxalato complexes

Of the several complexes of Cr(III) that can occur as anionic species the greatest emphasis was placed on the examination of the oxalato complexes. While the malanato, maleato and citrate complexes are capable of forming anionic complexes, as shown by simple radiotracer studies, the oxalato were chosen for further examination because their chemistry is well documented[216], they can be prepared in reasonably pure forms[161] and it seemed that they could serve as a simple but realistic model for the kinds of complexes of chromium expected in real systems.

The reactions of aquated Cr(III) with the oxalato anion may be represented by the equations:

$$Cr^{3+} + C_2O_4^{2-} \rightleftharpoons Cr(C_2O_4)(H_2O)_4^{+} \qquad (B.6)$$

$$Cr(C_2O_4)(H_2O)_4^{+} + C_2O_4^{2-} \rightleftharpoons Cr(C_2O_4)_2(H_2O)_2^{-} \qquad (B.7)$$

$$Cr(C_2O_4)_2(H_2O)_2^{-} + C_2O_4^{2-} \rightleftharpoons Cr(C_2O_4)_3^{3-} \qquad (B.8)$$

The equilibrium constants for these reactions indicate that the complexes are very stable at 25° C: log $K_{B.6}$ = 5.34, log $K_{B.7}$ = 5.17 and log $K_{B.8}$ = 4.93.[217] The rate constants have also been reported and are: $k_{B.6}$ = 2.82 x 10^{-3} s^{-1}, $k_{B.7}$ = 3.10 x 10^{-4} s^{-1} and $k_{B.8}$ = 1.05 x 10^{-4} s^{-1}.[218]

If present in natural waters, waste waters or biological fluids, could complexes of chromium such as these be distinguished from other forms of chromium by the current separation/speciation methods? In particular, is it possible that anionic Cr(III) complexes are confused with anionic Cr(VI) or missed in the identification of the Cr(III) species? Certainly, speciation techniques are suspect if they do not consider such complexes.

While it has been shown that anionic Cr(III) complexes are not precipitated when speciation is attempted using the iron (III) hydroxide coprecipitation technique[65,66], thus giving a false indication of the proportion of Cr(III) and Cr(VI) if all Cr(III) is assumed to precipitate, there are still claims that ion-exchange procedures are effective in speciation studies provided that there is no need to remove the chromium from the resin for analysis.[47] However, synthesized $^{51}Cr(C_2O_4)_3^{3-}$ was trapped on anion-exchange resins but passed through cation-exchange resins every bit as well as did anionic Cr(VI). In fact, by following the label radiometrically it was possible to study the effects of eluting reagents just as was done for the CrO_4^{2-}. While water did not move this band at all there was some slight displacement by 0.5M KCl solutions but not a measurable amount by 0.1M KCl solutions. Solutions of 0.5 M Na_2SO_4 caused little movement and 0.5M K_3PO_4 caused no measurable displacement. Most of the complex was destroyed and removed by 5M $HClO_4$, 6M HCl or 9M H_2SO_4. In a like manner, $Cr(C_2O_4)_2^-$ was exchanged on AG1-X4(Cl^-) resin. However, it could be displaced readily by 0.5M KCl or Na_2SO_4 and even slowly by 0.1M salt solution.

In light of these experiments it would seem difficult to unambiguously distinguish between Cr(VI) and anionic complexes of Cr(III) by ion-exchange procedures alone. Yet, Orvini and Gallorini[47] claim that in the analysis of river waters at pH 5.5 a sequential use of AG50W-X4(H^+) resin then AG1-X8(OH^-) resin permits Cr(III) and Cr(VI) determinations. Their statement that "the AG50 resin fixes all the Cr(III) ions in solution, while the Cr(VI) chromate ions pass to the next AG1 column, where they are completely retained" seems possible only if they have been able to pass Cr(VI) quantitatively through a cation-exchange column, something that proved to be very difficult in this research program, and only if all of the Cr(III) in the river waters was cationic. With respect to complexing agents, including oxalic acid, they report that "only high concentrations of these reagents" affect the results. This may be true in the short run, particularly with low reagent concentrations, since the rates of the reactions of Cr(III) with complexing agents such as $C_2O_4^{2-}$ are very slow. Nevertheless, at equilibrium some Cr(III) should be complexed and all need not remain cationic. It would seem judicious for them to claim a reasonable separation of cationic and anionic chromium, rather than speciation.

On the other hand, the solvent extraction of Cr(VI) by DPPM is very effective and quite different from the non-extraction of the anionic oxalato complexes of Cr(III) (Sectio 4.3). There can be no confusion of these two different forms of chromium as is possible with ion-exchange procedures. However, anionic Cr(III) complexes are known to be extracted by some extractants.[150] Why will the anionic Cr(III) oxalato complexes

not separate from the aqueous 1M HCl phase into the DPPM/diluent? Although it seems improbable from the studies in 1M $HClO_4$[219,220,221], and in various HCl solutions[221], the possibility that the complexes such as $Cr(C_2O_4)_3^{3-}$ are rapidly aquated in 1M HCl was checked. Otherwise there must be some inhibition in the formation or extraction of the ion-pair composed of $DPPM^+$ and the anioic complex.

In a procedure similar to that employed by Banerjea and Mohan[219] and Bunton et al.[221] the dissociation of $Cr(C_2O_4)_3^{3-}$ in 1M HCl at room temperature was followed spectrophotometrically. The initial absorption spectrum in the acid was almost identical to that found for pure $Cr(C_2O_4)_3^{3-}$ dissolved in water while at an extended time it approached that of $Cr(C_2O_4)_2^-$. Data for this experiment is summarized in Table B.2.

TABLE B.2

Aquation of trisoxalatochromium (III) anion.

[HCl] = 1.0M, $[Cr(C_2O_4)_3^{3-}] = 1.0 \times 10^{-3}$M, Temp = 23±2°C, λ=420nm

Time (min)	A_t	$\ln (A_t-A_\infty)/(A_o-A_\infty)$
0	0.0990	0
13.3	0.0984	-0.0264
23.3	0.0981	-0.0399
33.3	0.0980	-0.0445
46.7	0.0975	-0.0674
58.3	0.0971	-0.0862
80.0	0.0961	-0.1348
95.0	0.0960	-0.1398
156.7	0.0938	-0.2563
4120.0	0.0760	
∞	0.0760	

After examining the respective absorbance spectra at 420 nm (A_o = original, A_t = time t and A_∞ = 4120 min) a least squares fit of the data $\ln(A_t-A_\infty)/(A_o-A_\infty)$ against t provided for a slope of -0.00161 min^{-1} with r = -0.996. The pseudo first order rate constant would then be $k = 2.7 \times 10^{-5}\ s^{-1}$, in good agreement with the literature value of $2.59 \times 10^{-5}\ s^{-1}$ in 1M HCl at 25° C.[221] Since the oxalato-Cr(III) complexes remain anionic their non-extractable nature must be due to the failure in the formation of an extractable ion-pair with DPPM rather than any decomposition.

Labelled Cr(III)- oxalato complexes were also used to prove that Ce(IV) was an effective oxidant for these species as well as for aqueous Cr(III). Teggins et al.[222] have examined such reactions at mM concentrations in H_2SO_4 in some detail. They point out that the coordinated oxalate must be oxidized as well as the Cr(III). Thus, it might be expected that not only would more Ce(IV) be required but the rate of reaction could be slower than with aqueous Cr(III). However, as long as Ce(IV) was in excess the oxidation to Cr(VI) was satisfactory within 30 minutes at room temperature.

APPENDIX C

Extraction of Metals

The DPPM extraction of a number of metallic species was examined, with particular attention focussing on any problems such extractions would cause in the analysis of Cr(VI). The influence of iron is of concern since it often occurs in solution with chromium. The effects of both cerium, Ce(IV), and manganese, Mn(VII), are of interest because they may be used in the oxidation of Cr(III). The extraction of other elements which may form anionic chlorocomplexes is of interest because the extent to which Cr(VI) may be separated from some such elements by a DPPM extraction has been explored only in a limited manner so far.

The extraction of these metallic species was investigated by spectrophotometric methods or by radiotracer techniques following the procedures described in the examination of the Cr(VI). Table C .1 summarizes the properties of the radioisotopes monitored.

Table C .1

Properties of Radioisotopes

Isotope	Half-Life $t_{\frac{1}{2}}$	γ-radiation monitored (Mev)
^{51}Cr	27.8 d	0.320
^{64}Cu	12.8 h	0.511
^{65}Zn	245 d	1.11
^{115}Cd	54 h	0.523
^{115m}In	4.5 h	0.336
^{141}Ce	32.5 d	0.145
^{198}Au	2.7 d	0.412

Fe(III)

Extractions of iron from solutions containing chloride involves the complex $FeCl_4^-$, this anionic species forming to a greater extent as the concentration of HCl increases in the solution[140-145]. The extraction by 0.10M DPPM/$CHCl_3$ from 1 M HCl has been examined and it has been shown that the separation factor $\alpha = D_{Cr(VI)}/D_{Fe(III)} > 10^5$ [74]. On the other hand, extraction of Fe(III) by 0.10M DPPM/benzene from 7.0M HCl is much more effective than the extraction of Cr(VI) [223]. This evidence that the use of diluents other than chloroform can lead to a more efficient extraction of Fe(III), and the fact that the possible concentration of Fe(III) far exceeds that of Cr(VI) in most natural aqueous systems or effluents, dictates that the extraction of Fe(III) be explored.

To examine the influence of Fe(III) on the extraction of Cr(VI) a 30 mL solution which was 1.0M in HCl and containing 0.1 ppb Cr(VI) (as ^{51}Cr) and 3.3 ppm Fe(III) was extracted with 2.0 mL of 0.10M DPPM/$CHCl_3$. Radioassays proved that there was a negligible change in the extraction of Cr(VI) from that of a solution containing no iron. The ETA-AAS analysis of the organic extract was not influenced by the Fe(III). In chloroform as a diluent a concentration of Fe(III) at 33000 x that of the trace Cr(VI) does not interfere with the analysis.

The extraction of Fe(III) was examined spectrophotometrically using a different diluent, CH_2Cl_2. The initial solution was prepared with 62.5 ppm Fe(III) in 0.60 M HCl. This solution had an absorption maximum at 335 nm with a molar absorptivity of 1430 $M^{-1}cm^{-1}$ - a spectrum which could be expected from the information published by Desesa and Rogers [213]. After extraction by an equal volume of 0.10 M DPPM/CH_2Cl_2 the absorbance in the aqueous phase decreased by 1.9% and there was a corresponding increase in the organic phase.

Using the distribution ratio D = 0.02 for Fe(III) the separation factor with respect to Cr(VI) would be $\alpha = D_{Cr(VI)}/D_{Fe(III)} = 17500$.

It could be concluded that for the diluents which lead to effective extraction of Cr(VI) there should be no interference in most analyses of chromium, but scrubbing is advantageous in the spectrophotometric analysis of solution containing high Fe(III) concentrations (Appendix A3).

Mn(II)-Mn(VII)

While it has been shown that $KMnO_4$ is effective in oxidizing Cr(III) only in a time consuming procedure involving heating and the use of sodium azide, the influence of both Mn(II) and Mn(VII) on the Cr(VI) extraction were explored anyway. In a concentration which was 33000 x that of Cr(VI) the Mn(II) neither interfered with the extraction of Cr(VI) from 1.0 M HCl into 0.10M DPPM/$CHCl_3$ nor did it cause difficulties in the subsequent analysis by ETA-AAS. This is in keeping with expectations since the separation factor $\alpha = D_{Cr(VI)}/D_{Mn(II)} > 10^{6.74}$

$KMnO_4$, at a concentration of 5×10^{-3}N, did cause difficulties in an extraction from 1M HCl into 0.10M DPPM/CH_2ClCH_2Cl. First, the purple color of $KMnO_4$ in the aqueous phase disappeared quickly when shaken with the organic extractant. The organic phase took on a pale yellow color, possible due to the extraction of MnO_2 which could be formed in this system. Using a $^{51}Cr(III)$ label it was confirmed that as expected no Cr(III) could be oxidized at room temperature to be potentially extracted in this system. Further, with $^{51}Cr(VI)$ the extraction did not approach the extent expected from the known results in the absence of $KMnO_4$. The distribution ratio is lowered for Cr(VI) in the presence of Mn(VII), possibly because some of the extractant is tied up by the manganese complexes formed in the system or because the Cr(VI) complex in the aqueous phase is modified.

This investigation does suggest that if $KMnO_4$ is used to oxidize Cr(III) there must be extreme care taken if the extraction of Cr(VI) is to achieve its potential.

Ce(IV)

Ce(IV) is unquestionably the best of the oxidizing agents investigated for converting trace concentrations of Cr(III) to Cr(VI) under ambient conditions. As a consequence, both Ce(IV) and Ce(III) will be present in any solution to be extracted by DPPM. While it is known that for extraction from a 1.0M HCl solution the separation factor $\alpha = D_{Cr(VI)}/D_{Ce(III)} > 10^6$ when using 0.10 M DPPM/$CHCl_3$ [74], the extraction of Ce(IV) has not been investigated. Obviously some Ce(IV) is extracted since there is a pale yellow coloration in the organic phase when it is added to the aqueous phase in an extraction experiment.

To determine the extent to which Ce(IV) is extracted by DPPM/diluent the preparation of radioisotopes of ceruim was undertaken so that radiotracer studies could be completed. The (n,γ) reaction on both ^{140}Ce and ^{142}Ce can produce appropriate radioisotopes but the ^{141}Ce radioisotope was chosen for most studies. A sample of the Ce radioisotopes, prepared in the McMaster University Nuclear Reactor by irradiating a stock solution of Fisher Certified N/10 Ceric sulfate solution, was separated promptly on ion-exchange resins. Although the ion-exchange properties of cerium were not explored in detail, it was evident that in the irradiated solution which was 1.0 N in H_2SO_4, most of the γ-activity appeared in the cationic form of the element. The activity of the eluent from the AG 50W-X4 (H^+) cation resin was between 8.7 and 9.0% of that from the AG1-X4(SO_4^{2-}) anion resin - ie. over 90% of the ^{141}Ce and ^{143}Ce was cationic.

The solvent extraction from HCl solutions using 0.10M DPPM/CH_2ClCH_2Cl was investigated. 5.1 mL of an aqueous 1.2M HCl solution, containing 1×10^{-3}M

Ce(IV) as a carrier in addition to the radiolabelled cerium, was equilibrated with 2.0 mL of the organic extractant. An extraction using equal volumes of each phase from a 1.0M HCl solution was checked as well. For the labelled cerium it was determined that the distribution ratio never exceeded 0.05 and was generally much lower. However, there was a yellow tinge in the organic phase suggesting that more Ce(IV) was extracted than implied by the distribution of the radiolabelled substance.

From these results it seems probable that the nuclear bombardment is responsible for the reduction of some Ce(IV). Since the bulk of the material apparently remains as Ce(IV) it suggests that a Szilard-Chalmers reaction occurs in this system. While this is of obvious interest it would open up a totally new research project and was not examined.

Since a limited attempt to examine the extraction of the radiolabelled cerium from an HCl solution after the recommended oxidation by $K_2S_2O_8$ in the presence of an Ag^+ catalyst [224] proved to be of little success, it was decided that a brief spectrophotometric investigation could be of value. While the characteristics and spectrum of Ce(IV) in sulfuric acid are well documented [210, 224], this is not true in HCl where there is a reduction problem [169]. At this time most results must be regarded as preliminary. However, it does seem that the absorption maximum in HCl is shifted to a slightly longer wave length, near λ = 340 nm, than the λ max = 320 nm in H_2SO_4. After extraction by DPPM the absorption maximum in the CH_2ClCH_2Cl diluent is at even a longer wavelength, λ = 406 nm. The changes in absorbance with time could be followed and with a half-life in excess of 15 min. it is clear that the rate of reduction is much slower in the organic diluent than in the aqueous phase from which the extraction takes place. This may reflect the fact that while the concentration of HCl is about 1.0M in the aqueous phase it

is much less in the CH_2ClCH_2Cl, and most of the HCl there in is tied up as the ion-pair $\overline{DPPMH^+Cl^-}$.

Even though the characteristics of Ce(IV) in this extraction system are not yet fully understood, there is no doubt that it can be employed in the oxidation of Cr(III) without interference in any subsequent extraction and analysis of the Cr(VI) by AAS methods. In the spectrophotometric analysis of Cr(VI) in an extract it must be at present avoided. Either an alternative oxidation procedure must be employed or excess Ce(IV) must be destroyed before extraction. Alternatively, if the chromium analysis using peroxychromic acid is satisfactory, simple addition of H_2O_2 will both destroy the Ce(IV) in the extract and form the Cr(VI) complex.

Au(III)

It is well known that gold may form anionic complexes such as $AuCl_4^-$, $Au(NO_3)_4^-$ and $Au(SO_4)_2^-$ which are extractable by basic extractants[121,225]. While the DPPM/$CHCl_3$ extraction of gold has been studied[121] there has not been an examination of diluent effects. This would be of interest for comparison to the situation with Cr(VI). Changing the nature of the anion in the acidic aqueous solution and varying the gold concentration could also be informative. ^{198}Au, of high but undesignated specific activity, was obtained from the McMaster University Health Physics Laboratory for these investigations.

The distribution of Au(III) between the aqueous and organic phase was followed radiometrically. Samples were equilibrated for three minutes, centrifuged, separated and counted. The volumes used and counting times were chosen to minimize the counting error yet remain practical.

Using 0.10 M DPPM/diluent and extracting trace amounts of ^{198}Au(III) from a 0.97M HCl solution the distribution ratios were obtained for a number of diluents

Diluent	CH_2ClCH_2Cl	CH_2Cl_2	$CHCl_3$	$CHCl{=}CCl_2$	CH_3CCl_3	CCl_4
log D	3.6±0.1	3.4±0.1	3.1±0.1	1.86±0.02	1.79±0.02	0.67±0.01

Obviously, Au(III) is extracted more readily than is Cr(VI) with all of the DPPM/diluent solutions. However, the diluent effect must be similar in each case because the order of extraction for both Au(III) and Cr(VI) is identical. While the dielectric constant may be of some importance in determining this order there is a necessity to consider the hydrogen bonding capability of the diluents as well. Certainly, in this instance the chloroform like diluents are excellent for the extraction of what would be expected to be a large halometallic complex ion. This is a direct contradiction to Diamond's suggestion[118] that the chemically more inert non-polar diluent should favor the extraction of this large ion from the HCl solution by an amine extractant. However, DPPM may not act like all amines. According to the model, it is the distribution of the DPPM complexes between the two phases and the formation of the ion-pair complex in the aqueous phase, which in this case must be particularly stable and aquophobic, which determines the ultimate distribution ratio.

The extractions of gold from several aqueous acids, near 1M in acidity, by 0.100M DPPM/CH_2ClCH_2Cl were examined. The distribution ratios, D, were similar for extractions from HCl, HBr, HNO_3 and H_2SO_4. It is probable that the anionic gold complex found in these acidic solutions forms a very stable complex with the protonated DPPM and is removed to the organic phase as an ion-pair; eg. $DPPMH^+AuCl_4^-$. The anion of the acid itself cannot compete very well with this large aquophobic gold complex in the formation of a stable and extractable ion-pair. Extraction from $HClO_4$ was about one order of magnitude poorer than from the other acid (logD = 2.14 from 0.928M $HClO_4$). From the previous work it had been shown that the ClO_4^- anion at such concentrations competes very well

with other anions and ties up virtually all of the $DPPMH^+$. One would expect that the Au(III) extraction should be suppressed. Obviously it is to some extent, but Au(III) still competes well for the protonated extractant. By comparison, the Cr(VI) species in HCl solutions is extracted nearly as well as Au(III). In other acids Cr(VI) is extracted poorly and in $HClO_4$ only infinitesimally, certainly many orders of magnitude poorer than from HCl solutions. This is a further indication that the CrO_3Cl^- species suggested in this study as being most important in HCl solutions is extracted more favourably than is the $HCrO_4^-$ species thought to be present in $HClO_4$ solutions.

The influence of the concentration of DPPM/CH_2ClCH_2Cl on the distribution ratio of Au(III) from 0.96M HCl solution was examined. A value of log D = 0.17 was found for the pure diluent. Using 1×10^{-3} to 1×10^{-1} M DPPM/CH_2ClCH_2Cl to plot of log D vs. log [DPPM] for the extraction is shown in Figure C1. This graph has a slope of 0.63 with a correlation coefficient of 0.98, in marked contrast to a slope which changes from two to one, depending on the [DPPM], reported for the study with DPPM/$CHCl_3$.[121] Certainly in CH_2ClCH_2Cl there is no need to invoke the mixed quadropoles, the double hydrogen bonding or the complexes of metal acids to account for the situation as was done in the $CHCl_3$ diluent[121].

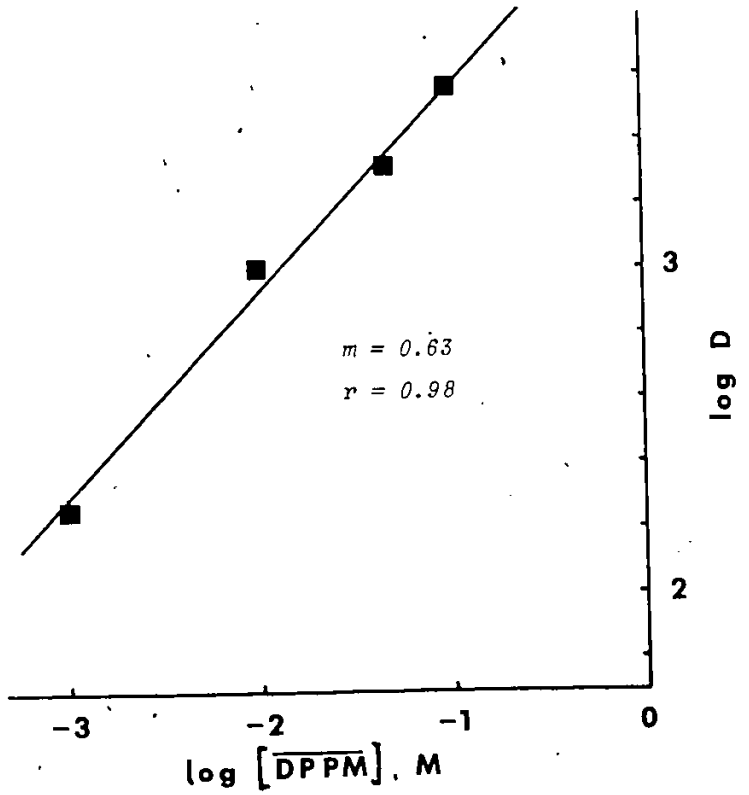
The extraction using 0.10M DPPM/CH_2ClCH_2Cl with different concentrations of HCl in the aqueous phase was examined. Results may be summarized as:

log[HCl]	-1.196	-0.903	-0.225	-0.019	-0.018	+0.669
log D	3.31	3.31	3.44	3.58	3.57	3.50

While carried beyond significance to better show the trends, these distribution ratios do indicate that the extraction is very much favored over a wide acid concentration range. Not only is the distribution ratio

Figure C.1

The variation in the extraction ratio, D, for the extraction of Au(III) in 0.96 M HCl by different concentrations of DPPM initialy present in the organic diluent CH_2ClCH_2Cl.


m = 0.63
r = 0.98
log D
3
2
-3
-2
-1
0
log [DPPM], M

significantly greater than reported in $CHCl_3$, but it does not appear to drop off dramatically above 0.25M in HCl.[121]

A number of other properties of Au(III) were checked with a comparison to Cr(VI) in mind. A change in the equilibration time or in the concentration, from trace to millimolar Au(III), has no appreciable effect on the distribution ratio; contrast this with the results for different equilibration times of oxidatively unstabilized Cr(VI) at different concentrations. There is little loss of Au(III) from the organic extractant system upon standing for weeks. Since little radioactivity appears on the container walls the Au(III) must remain as a stable complex in the organic phase. Ion-exchange experiments confirmed that the Au(III) occurred as an anionic species in not only HCl but also in HNO_3 and $HClO_4$ solutions. These points support the supposition that the extraction proceeds with a formation of a stable $DPPMH^+AuX_4^-$ complex.

The extraction of Au(III) was examined spectrophotometrically. In 0.60M HCl in the μg/mL (ppm) concentration range the Au(III) exhibited an absorbance maximum at 313 nm with a molar absorptivity of about 5000 M^{-1} cm^{-1}. A single extraction by an equal volume of 0.100M DPPM/CH_2Cl_2 reduced the absorbance in the aqueous phase by approximately 99%. The absorbance in the organic phase was then examined. There was a shift in the absorbance maximum to 329 nm and an increase in the molar absorptivity to about 7170 M^{-1} cm^{-1}, assuming that the extraction was nearly quantitative. Although the absorbance was significantly less at 364 nm, where Cr(VI) would be monitored, the extraction of gold could interfere somewhat with a spectrophotometric analysis of Cr(VI) employing a DPPM extraction.

Zn(II), Cu(II), Cd(II), In(III)

A considerable amount of information on the extraction of chlorocomplexes of certain metals by basic extractants is available in the

literature[226,227,228]. The extraction of a number of metals from HCl solutions employing DPPM/$CHCl_3$ has even been investigated by Ejaz et al[74,121]. Of interest are the reported separation factors:

$D_{Au(III)}/D_{Cu(II)} = 10^5$ for 0.25 M HCl and 1.0 M HCl

$D_{Cr(VI)}/D_{Cu(II)} = 10^5$ for 1.0M HCl

$D_{Au(III)}/D_{Zn(II)} = 10^5$ for 0.25M HCl but 10^2 for 1.0M HCl

These data indicate that Cu(II) has a low distribution ratio for DPPM/$CHCl_3$ over a range of HCl concentrations but Zn(II) is extracted better at higher HCl concentrations. These types of extraction warrant further investigation of the acid effect and diluent effect. Also, it is possible that the more toxic Cd(II) could be extracted even better than Zn(II).

Radiotracer techniques could prove advantageous in investigating the extraction of metal chlorocomplexes. Because of an experiment in the laboratory to produce carrier free copper isotopes by the (n,p) reaction on zinc, a number of isotopes became available: ^{65}Zn, ^{64}Cu, ^{115}Cd and ^{115m}In. The zinc, irradiated in a cadmium envelope, was dissolved in HCl. This solution was the source of ^{65}Zn and ^{64}Cu. A small amount of the cadmium envelope was also dissolved in HCl. This solution provided the ^{115}Cd and the decay product ^{115m}In for the radiotracer experiments. The standard extraction and counting techniques developed in this program were utilized.

The dependence of the distribution ratio for zinc when extracted by 0.100M DPPM/diluent from hydrochloric acid solutions of various concentrations is shown in Figure C.2. Both the acid effect and diluent effect are apparent. Zinc is extracted most effectively when the HCl concentration is about 3M. The increase in the distribution ratio up to this concentration of HCl probably reflects both the increase in the concentration of the protonated extractant and of the extractable anionic zinc complex in the aqueous solution. Beyond 3M

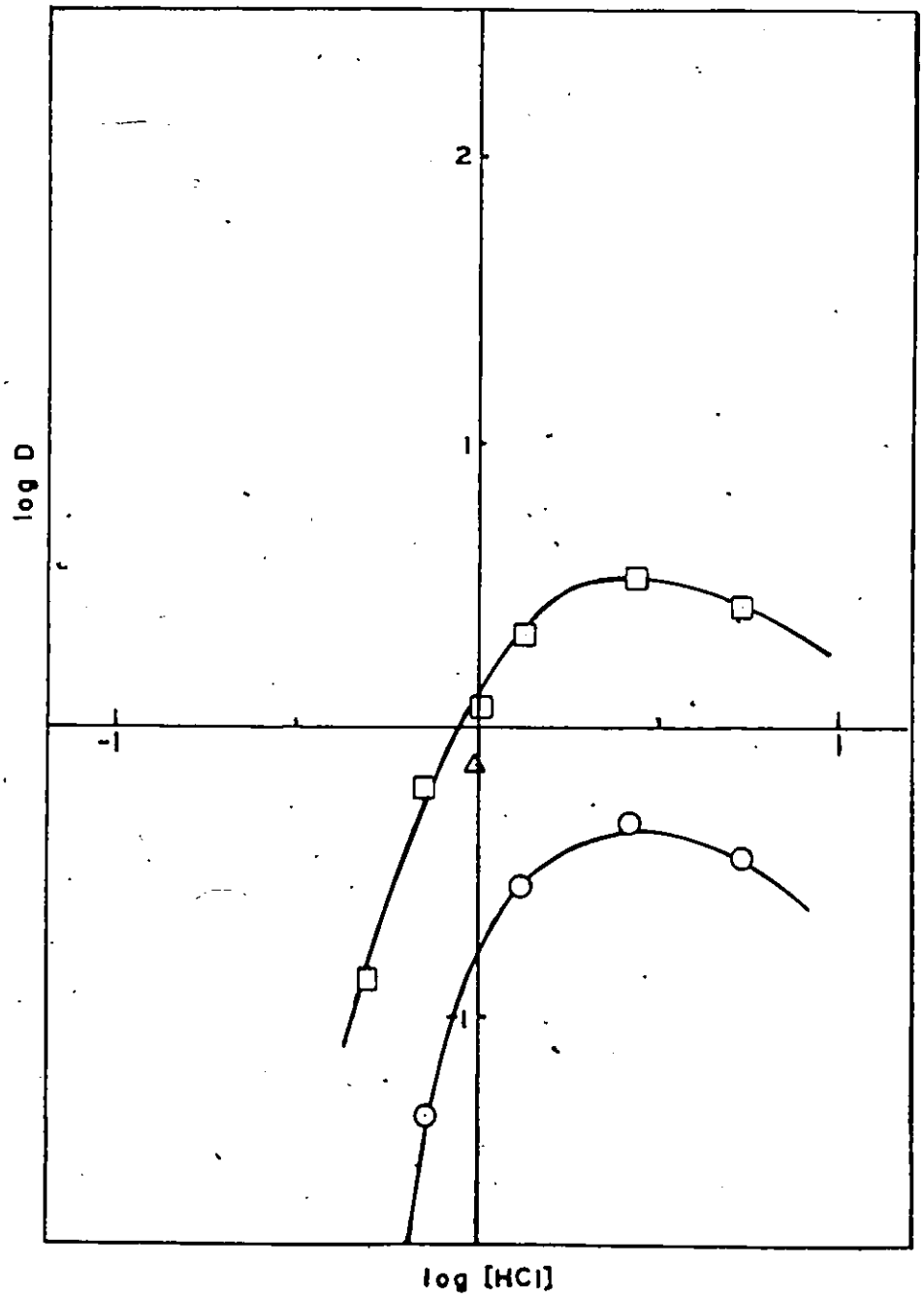
Figure C.2

The extraction of Zn(II) from HCl solutions by 0.1 DPPM/diluent. The distribution ratio of zinc as a function of the acid concentration is depicted for the extraction by:

0.10M DPPM/$CHCl_3$ ○

0.10M DPPM/CH_2Cl_2 △

0.10M DPPM/CH_2ClCH_2Cl □


2
1
log D
-1
1
-1
log [HCl]

HCl the competition by chloride for the ion-pair sites or a destruction of the anionic zinc complex must occur. These possibilities were checked by adding to a sample which was kept 1.0M in HCl vardous amounts of LiCl. A nearly linear increase in the distribution ratio with total chloride concentration resulted (Figure C3). Initially the slope of this graph was somewhat lower than for the addition of HCl with the same chloride concentration. This indicates that the extractant protonation does have some effect on the extraction beyond 1M in H^+. However, once reasonable protonation has been achieved the addition of LiCl leads to an almost as rapid increase in D with no apparent eventual decrease, at least up to the concentration examined. Therefore, the principle phenomenon determining the extractability involves the formation of the anionic zinc chloro-complex in the aqueous solution. At higher concentrations it is probable that a change in the anionic chloro-complex in the presence of high acidities has a greater influence on the lowering of the extraction than does any competition by chloride ions for the pairing sites.

For the zinc extraction a plot of log D vs. log [DPPM] provides a nearly linear relationship with a slope near 1.5 (Figure C4). This suggests that the extraction is of mixed complexes such as $ZnCl_3^-$ and $ZnCl_4^{2-}$. Such complexes are probably the major extractable species in HCl solutions[229,230,231].

It was apparent that copper extracts only poorly into DPPM/diluent from a solution of hydrochloric acid. A few spot checks indicated that even zinc could be separated more readily than copper, $\alpha = D_{Zn}/D_{Cu} \geq 10^3$. Since copper should pose no difficulty in any analysis of Cr(VI) involving a DPPM extraction, experiments with this metal were pursued no further.

Cadmium is more readily extracted from an aqueous solution of HCl into DPPM/diluent than is zinc. The distribution ratio curves for cadmium as a function of the hydrochloric acid concentration are illustrated in Figure C5.

Figure C .3

The effect of added Cl^-, as LiCl, on the extraction of Zn(II) from a 1.0 M HCl solution by 0.10 M DPPM/CH_2ClCH_2Cl.

Figure C .4

The variation in the extraction ratio, D, for the extraction of Zn(II) in 1.2 M HCl by different concentrations of DPPM initialy present in the organic diluent CH_2Cl_2.

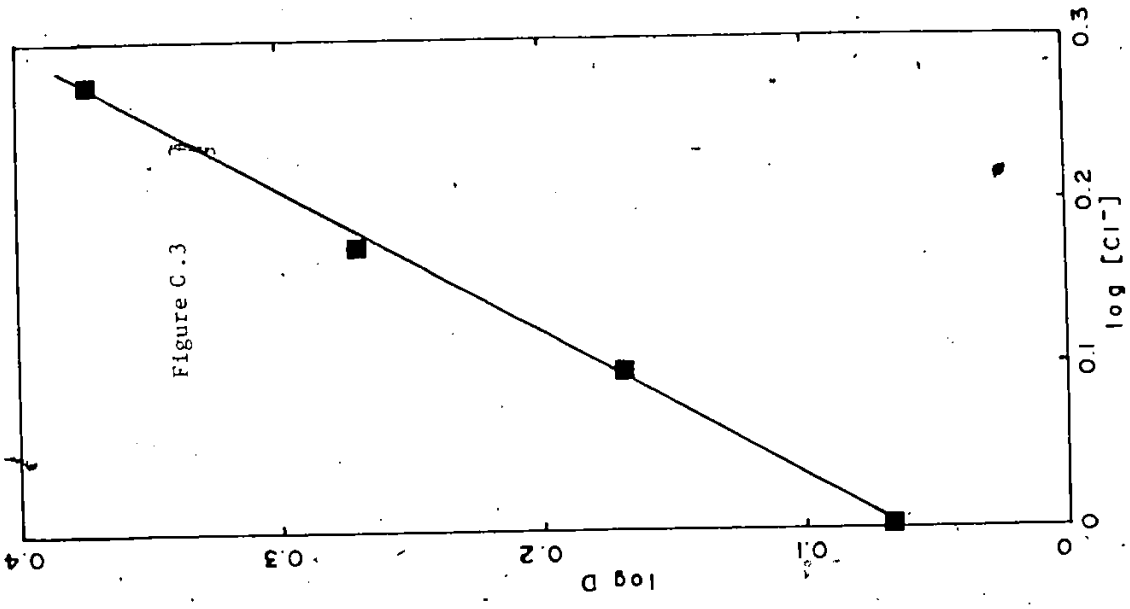


Figure C.3

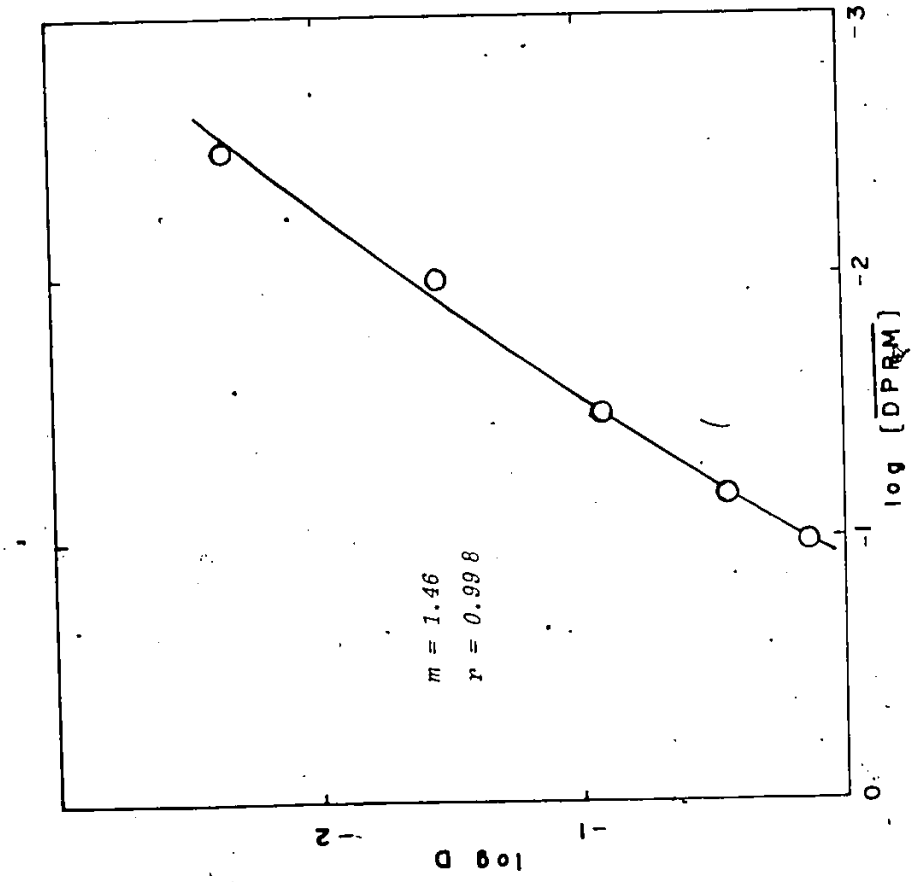


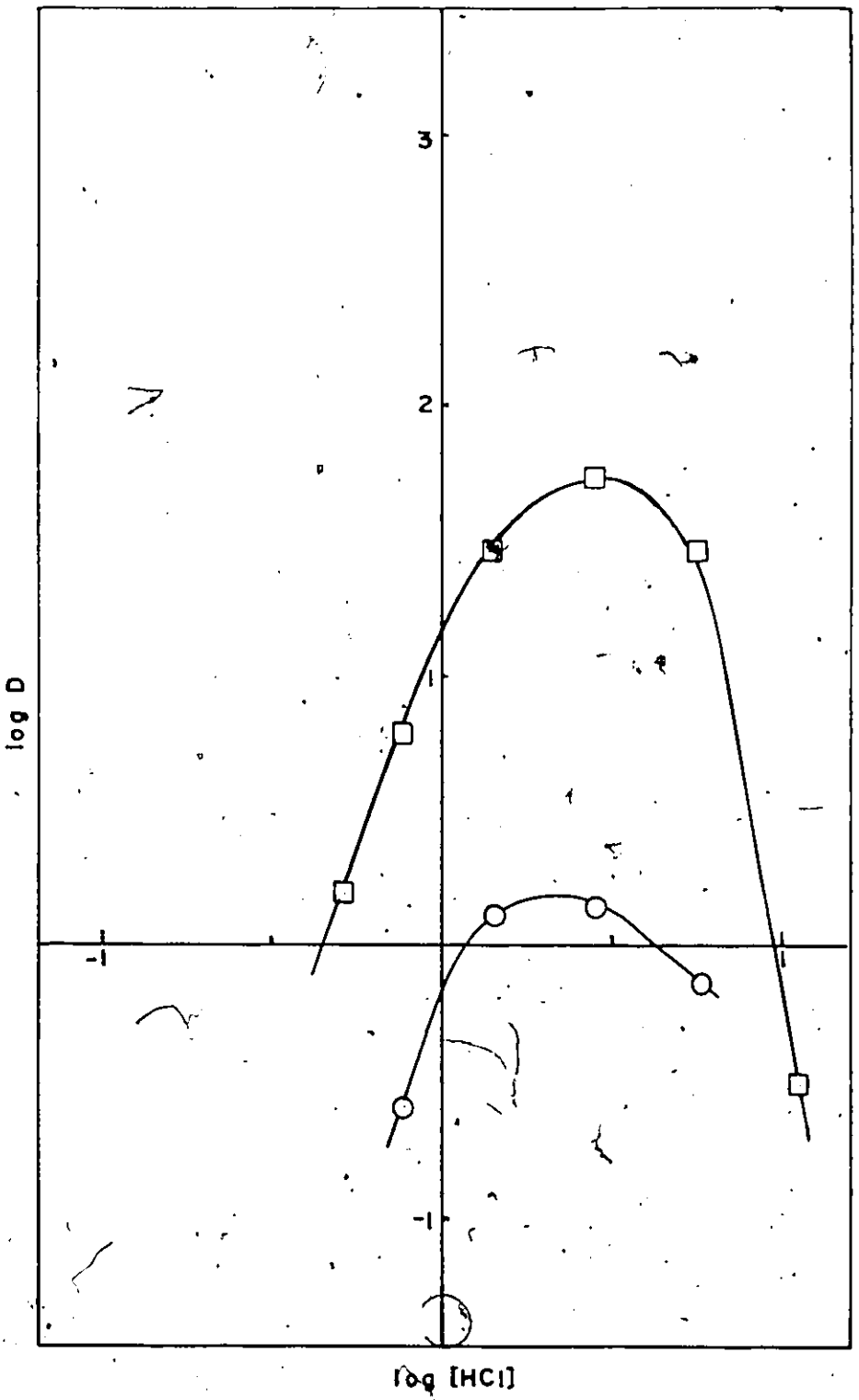
Figure C.4

Figure C. 5

The extraction of Cd(II) from HCl solutions by 0.10M DPPM/diluent. The distribution ratio of cadmium as a function of the acid concentration is depicted for the extraction by:

0.10M DPPM/$CHCl_3$ ○

0.10M DPPM/CH_2ClCH_2Cl □


3
2
1
-1
-1
log D
log [HCl]

It can be seen that with cadmium as well as zinc the extraction maxima are near 3M in HCl and there are similar diluent effects. The anionic cadmium complexes which form an ion-pair with $DPPMH^+$ and are extracted into the organic phase must be similar to those in the zinc solution. Generally, $CdCl_4^{2-}$ is thought to be extracted in such systems[231]. Since the cadmium complexes would be larger and more hydrophobic than the zinc complexes the distribution ratio would be larger.

Indium is not extracted preferentially into 0.100M DPPM/CH_2ClCH_2Cl until the hydrochloric acid concentration approaches 6M. As illustrated in Figure C6 the distribution ratio is subject to diluent effects as well as being dependent on the concentration of HCl. This extraction profile is somewhat different from the other elements examined radiometrically. Possibly the extraction involves the higher chloro complexes, $InCl_6^{3-}$ and $InCl_5^{2-}$, as well as $InCl_4^-$, as suggested by certain researchers[232,233].

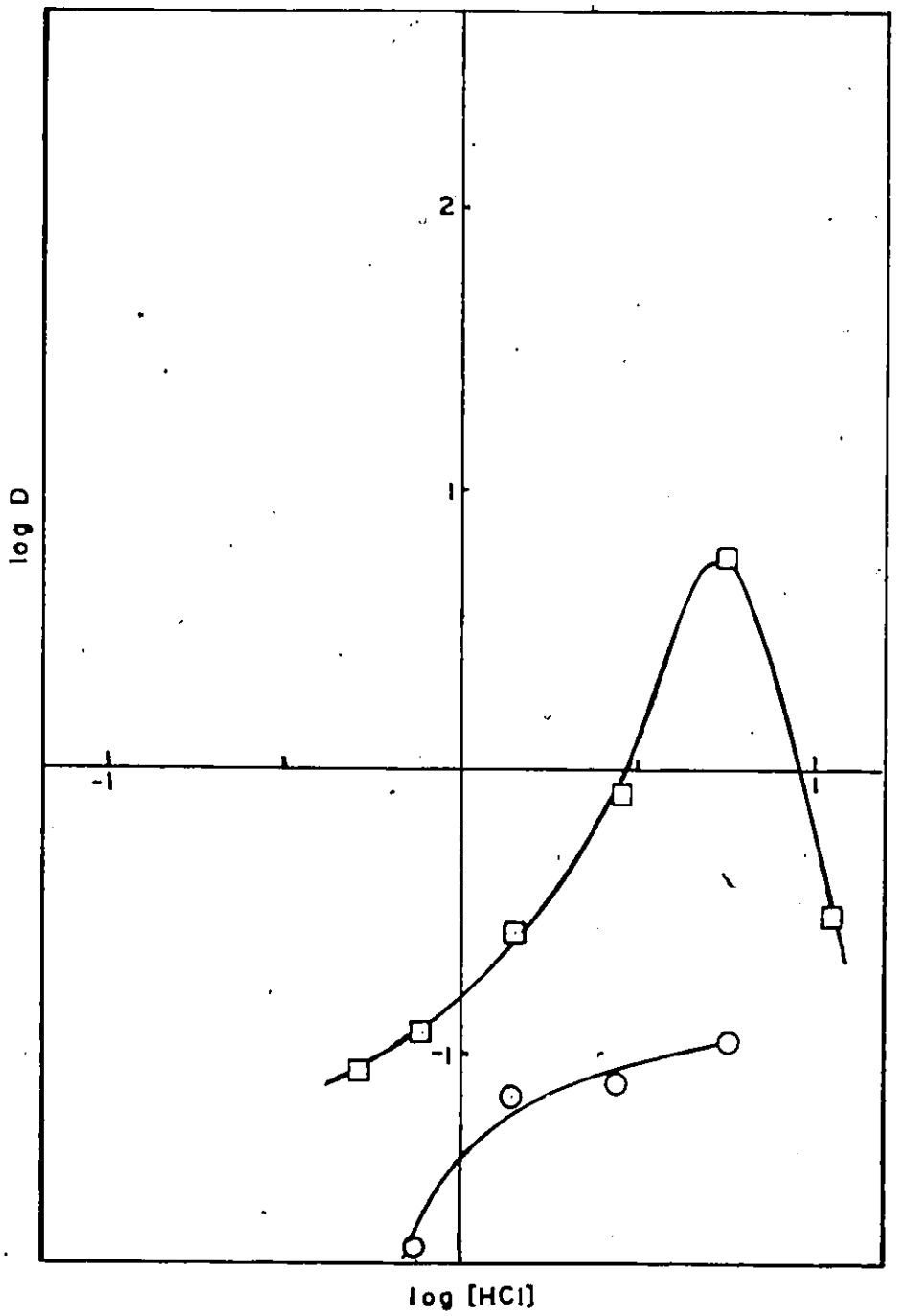
If there is a specific interest in the separation of the parent radioisotope ^{115}Cd from the daughter decay product ^{115m}In then the extraction system employing DPPM could be of significant value. For instances, using 0.100M DPPM/CH_2ClCH_2Cl the extraction of a solution containing ^{115}Cd and ^{115m}In at secular equilibrium in 1.44M HCl was explored. Since the distribution ratios are respectively $D_{Cd} \approx 28.9$ and $D_{In} = 0.25$ under these conditions, there is a reasonable initial separation of the two metals. After scrubbing the organic phase contains only the cadmium in any significant quantity. This separated organic phase was stored by itself or in contact with an equal volume of the pure HCl solution and allowed to decay. In any subsequent extraction since 97% of the cadmium remains in the organic phase there was almost pure ^{115m}In in the aqueous phase as indicated by the γ-counting. Although not explored in depth this use of a DPPM extraction proved satisfactory in not only

Figure 6

The extraction of In(III) from HCl solutions by 0.10M DPPM/diluent. The distribution ratio of indium as a function of the acid concentration is depicted for the extraction by:

0.10M DPPM/$CHCl_3$ ○

0.10M DPPM/CH_2ClCH_2Cl □


2
1
-1
1
-1
log D
log [HCl]

separating these two metals and preparing carrier free ^{115m}In but also in following the decay of ^{115}Cd and formation and decay of ^{115m}In.

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