THE INTERACTION OF HUMIC ACIDS FROM
TASMANIAN PODZOLIC SOILS WITH
MINERALS AND THE PROPERTIES OF
THEIR METAL HUMATES

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This thesis contains no material which has been accepted for the award of any other degree or diploma in any university and, to the best of my knowledge and belief, contains no copy or paraphrase of material previously published or written by another person, except where due reference is made in the text of the thesis.

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CONTENTS

LIST OF TABLES

LIST OF FIGURES

ABSTRACT

The humic acids from podzolic soils of north-western and western Tasmania have the general chemical and optical properties of the group as described in the literature. They do not correspond closely to the humic acids of the classical Northern Hemisphere podzol in that they have higher C : H ratios and lower optical densities. In addition they provide a far higher proportion of the total humic substances than do the humic acids of the classical podzol.

All samples of humic acids extracted from the Tasmanian soils exhibit very strong solvent activity towards minerals, particularly those of economic deposits. For example, 50 ml of a 500 mg/l solution of the humic acids from soil developed under white topped stringybark (*Eucalyptus delegatensis*) and bracken fern (*Pteridium aquilinum*), extracted 2 500 µg of lead from 7.6 g of 0.3 to 0.6 mm diameter grains of galena in 24 hours. Even gold is soluble in solutions of humic acids and it is likely that the formation of gold humates is the important mechanism of transport of this metal in wet temperature climates.

The aggressive action of humic acids towards minerals in the experimental studies, leaves no doubt as to their potential in weathering. Since the minerals of economic deposits are highly vulnerable, the rapid degradation of sulphides and secondary minerals may explain the poor development of gossans over mineralisation in Tasmania during the current erosional cycle. The activity of humic acids presents a problem in geochemical prospecting since secondary dispersion patterns may be weakened or obliterated.

The mechanism of the interaction of humic acids with minerals and cations has been investigated by means of pH measurements, potentiometric

titration, polarography, x-ray diffraction, electrophoresis and
infra-red spectroscopy. All these indicate that complexation is an
important mechanism of reaction. Polarographic studies also suggest
that the most probable value for the standard reduction potential of
humic acids is about 0.7V. Reaction kinetic studies of several of
the rapid reactions between humic acids and minerals indicate that
the reactions involved are of first order.

The simple organic compounds of soils, such as amino acids for
example, are no more active in mineral degradation than are humic
acids. In view of the low concentration and rapid bacterial utilisation
of these compounds their contribution to weathering must be limited.
Waters enriched in CO_2 also appear less efficient as solvents than
humic acids, since on the basis of equivalent carbon contents the
latter are far more effective. From an extremely conservative estimate,
it appears that some 150 000 tonnes of humic substances flow to the
sea from an aggregate catchment of about 20 000 km^2 in western Tasmania
every year. Thus these substances have both the power and quantity to
play an important role in the wet temperate weathering cycle.

ACKNOWLEDGEMENTS

INTRODUCTION

In an early report on south-western Tasmania, Baker (1957) suggested that the extensive bleaching of the rocks in the area was caused by waters which drained through button grass (*Gymnoschoenus sphaerocephalus*) plains. The solvent power of such waters was made apparent by the observation that boiled drinking water, taken from a creek, completely corroded the tin plate from the water-air control of the storage boiler within a few hours.

During recent years the writer has had the opportunity to investigate the possible reasons for the activity of waters draining from various vegetation types in north-western and western Tasmania. To date the study has had three major facets, namely the extraction of humic acids from soils developed under a number of differing types of vegetation, the interaction of these substances with minerals and the characteristics of a number of metal humates. Chapters 1 and 2 of this thesis are concerned with the occurrence of humic substances, their characteristics and known activity in geological processes, as reported in the literature. Chapter 3 deals with the extraction of humic substances from several Tasmanian soil types and such of their characteristics as could be determined with the limited facilities available. In Chapter 4 the effect of the Tasmanian samples of humic acids on a wide variety of minerals, with emphasis on those associated with economic deposits, is examined. Comparisons are made with the simple organic compounds of soils and with CO_2 enriched waters. Chapters 5, 6 and 7 deal with the application of a variety of electrochemical, x-ray diffraction and miscellaneous procedures for the examination of the characteristics of metal humates. Some of these procedures are applied in Chapter 8 to an intensive study of interaction of gold with humic acids and the mobilisation of this metal under wet temperate conditions is discussed. Chapter 9 presents general summary and comment on the activity of humic acids in the geochemical cycle.

The investigations presented in this thesis are thus not so much concerned with what humic substances are but what they are likely to do. No research project is without its problems and in the case of humic acids there are often more problems than answers. In making reference to these substances Breger (1970) commented "It is not difficult to see why such work has been pretty much neglected. Not only is the organic matter difficult to characterise, but it is also subject to continuing chemical reaction, dehydration, ageing and other phenomena which may be either reversible or irreversible. Avoidance of such work, because of its difficulty, cannot be severely criticised. To paraphrase a well-known quotation, "blame them not, for they know what they do not do." The writer has found this statement quite accurate. An attempt has been made to encourage humic acids to reveal the manner in which they operate in the geochemical cycle and it remains for the reader to ascertain if this has been successful.

CHAPTER 1

A BRIEF REVIEW OF THE OCCURRENCE AND CHARACTERISTICS OF HUMIC SUBSTANCES

1.1 Historical comment

Humus is a Latin word meaning ground or earth. The first

scientific use appears to have been made in Sweden by Wallerius

(1761) who applied the term to the decomposing plant materials of

soil. The Russian scientist and poet, Lomonosov (1763) noted that

the humus of soil originated from the slow rotting of plant and

animal residues with time. These views have become the accepted

definition of humus. Achard (1786) obtained organic concentrates

from humus by alkaline extraction of peat, and in the 100 years that

followed, similar materials were isolated from decomposing plants,

soils and waters.

Throughout early investigations, attempts were made to explain

the origin of humus, and Braconnot (1807) produced humus-like materials

which he named ulmin, by the action of mineral acids on carbohydrates.

Many other investigators of the period produced similar compounds by

the reaction of carbohydrates or cellulose with mineral acids and

alkalis. These were believed to be individual chemical compounds and

were given names and empirical formulae. Julien (1879), for example,

found 25 such compounds described in the literature to that time. In

attempts to justify their claims for the existence of these compounds,

the early investigators tended to emphasise the small compositional

differences between their products. This resulted in much confusion

in terminology and some investigators became sceptical of the

existence of humic substances.

German (1836), although constrained by the accepted views of

his time concerning chemical individuality, recognised that the

numerous substances extracted from humus and other sources could be

classified into groups which were respectively water soluble, alkali soluble and insoluble. Over 50 years later the investigations of Hoppe-Seyler (1889), Odén (1919) and Shmuk (1930) provided the basis for the currently accepted view that many substances found in humus are not individual compounds, but rather groups of substances displaying characteristic properties.

1.2 Terminology of humus

In this thesis the terminology applied to humus is essentially that used by Kononova (1966). The substances in humus fall into two major categories: they are either organic chemicals of individual nature which belong to the many recognised groups in organic chemistry, or they belong to a less well defined group referred to as humic substances. The chemically individual compounds are minor constituents and contribute up to 15% of the humus. In studies by Schreiner and Shorey over the period 1908 to 1930, more than 40 individual chemicals were identified in humus and some examples of these are parafin, oxalic acid, hydroxystearic acids, salicylaldehyde, vanillin, pentose and lysine.

The humic substances constitute the bulk of the organic reserves of the soil and they are generally divided into three sub-groups: humin, humic acid and fulvic acid. To consider each of these, further digression into historical aspects of soil science is necessary.

Humin. This is the alkali insoluble fraction of humus. It was originally referred to as 'humus coal' by Sprengel (1826) but the term humin, introduced by Berzelius (1839), is now preferred by soil scientists. Humin has been found to be largely a stable association of humic acid with soil mineral matter. Pre-treatment of soils with acid generally enables release of much of this fraction on subsequent alkaline extraction. In peaty soils, incompletely humified plant

residues are included with the humin fraction, and in other moist soils with restricted aeration carbonised plant residues may also contribute.

Humic acid. This is the alkali soluble, acid insoluble fraction of humus. Sprengel (1826) who recognised the acidic character of this fraction credits Döbereiner for the name 'humus acids'. Alexandrova *et al.* (1968) follow historical precedent in accepting this term although the majority of soil scientists favour the term humic acid introduced by Mulder (1862). Further subdivision of humic acid has been made. That portion soluble in ethanol is called hymatomelanic acid, a name which was introduced by Hoppe-Seyler (1889). Fractionation according to behaviour towards electrolytes has also been undertaken. Springer (1938) referred to that fraction remaining dispersed in the presence of electrolytes as *Braunhuminsäure* (brown humic acids) whilst the fraction precipitated was called *Grauhuminsäure* (grey humic acids).

Fulvic acid. The alkali soluble, acid soluble fraction of humus was named fulvic acid by Odén (1919). He considered this fraction to be equivalent to the humic substances occurring in waters which were named crenic and opocrenic acid by Berzelius (1833).

Numerous attempts have been made to produce chemically discrete fractions of humus by use of solubility in various organic solvents, chromatography, electrophoresis and gel permeation although the results have not been encouraging. Dubach and Mehta (1963) have commented that the fractionation appears to be endless and possibly no two molecules of humic substances are exactly alike.

1.3 *The nature of humic substances*

Wide differences of opinion are expressed about the nature of humic substances in the geochemical literature. Rankama and Sahama (1949) follow the concept of Waksman (1936) that humus forms as the

result of reaction between lignin, which is of direct plant origin, and proteins developed in the soil by microbial synthesis. Tyurin (1937) drew attention to the fact that Waksman's ligno-protein model for the generation of humus did not account for its production under extensive grasslands, which have low lignin content. Mason (1958) made reference to humus-colloids, and suggested that they are probably albumins whilst Krauskopf (1967) presented the view that humic acids are an ill-defined group of high molecular weight compounds, which are obtained by the digestion of wood in strongly alkaline solutions. Stevenson and Butler (1969) described humic substances as acidic, yellow to black coloured, moderately high molecular weight polymers which have characteristics dissimilar to any organic compounds occurring in living organisms.

Publications in soil science present more enlightened comment on humic substances. A thorough review of knowledge in this field of study has become available in the western world, by translation of monographs on soil organic matter by Kononova (1961, 1966). In these works, humic substances are considered to be complex, essentially aromatic heteropolycondensates of high molecular weight, produced by bacterial degradation and synthesis. Flaig et al. (1975) have presented a comprehensive review of the chemical and physical properties of humic substances. They follow views first expressed by Bromfield and Coulson (1959), and define humic acids as high molecular weight structureless polyanions formed mainly by polymerisation reactions involving phenolic and nitrogenous compounds.

From the preceding summary it is apparent that much geochemical comment on the nature of humic substances is of little value. The views of Rankama and Sahama (1949) are at least compatible with those expressed in more recent soil science literature. Whilst unaltered

lignin may not contribute directly to the formation of humic substances, the polyphenols resulting from degradation of lignin are certainly important in this respect. The suggestion of Mason (1949) that the humus colloids are albumins is not supported by reference to the significant properties or published data. The statement by Krauskopf (1967) that humic acids result from the digestion of wood in strongly alkaline solutions, is of historical interest only. As was noted in section 1.1 of this chapter, early concepts of humus formation were based on the action of mineral acids and alkalis on cellulose. The argument as to whether humic substances are natural components of the soil, or artifacts of the extraction procedures, was settled by Williams (1939) who made use of a lysimeter to demonstate their presence in drainage waters.

The humic substances are of extremely complex character and no simple definition is possible. The statements of Kononova (1961, 1966) stress the production of humic substances by means of poly-condensation reactions since these offer, where water is a by-product, a ready explanation of the variation in molecular weights with differing climates. She does not exclude the occurrence of poly-merisation reactions, however, which is the mechanism favoured by Stevenson and Butler (1969) and Flaig et al. (1975).

1.4 Properties of humic substances

A comprehensive review of the properties of humic substances is far beyond the scope of this thesis. Some comment is desirable, however, on those properties which are most likely to have a bearing on the interaction between these substances and minerals. Since humic substances are mixtures of comparatively large molecules their properties are either expressed as ranges or as average values.

Estimates of the molecular weight of humic substances have been made by a number of methods. Dubach and Mehta (1963) comment that cryoscopic and osmotic measurements yield erroneously low values,

of the order of 1000, whereas viscosimetry, ultracentrifugation and gel permeation techniques yield a range of 2000 to 300 000 with average molecular weights in the range 3000 to 50 000. Gel permeation has been widely used and with this method Dell' Agnola et al. (1964) found the molecular weight distribution of a humic acid extract over the ranges 0 to 4000, 4000 to 9000, 9000 to 100 000 and 100 000 to 200 000 to be 12%, 3%, 23% and 62% respectively. Using a number of the above noted methods Orlov et al. (1971) found that the weighted average molecular weights of humic acids ranged from 50 000 to 90 000 whereas fulvic acids had a lower and more limited range of 10 000 to 12 000. Whilst gel permeation studies provide useful data concerning humic substances, Söchtig (1975) has drawn attention to two problems. Firstly, the relationship between molecular weight and retention by dextran gels has been established with reference to globular proteins, which may not reflect the behaviour of humic substances and secondly, it is not certain that humic acids do in fact occur as molecules. For these reasons Söchtig (1975) used gel permeation data as an indication of relative particle sizes only. In a study of a podzol B horizon he used the maximum peak heights of the elution curves to establish the following relative particle sizes: total humic substances extract (nearly 9000), total humic acid (13 000), grey humic acid (20 000), brown humic acid (9000) and fulvic acid (4000).

Ranges in composition of fulvic and humic acids are given in Table 1 which also includes other properties of these substances. The C:H ratios indicate that fulvic acids have a lower aromatic content than do humic acids. This feature is also reflected in the light absorption characteristics of the fulvic acids since, as Kononova (1966) indicates, the higher the degree of condensation to aromatic structures in humic substances the greater their optical density.

Table 1. *RANGES IN COMPOSITION AND PROPERTIES OF FULVIC*
AND HUMIC ACIDS*

		Fulvic acids	Humic acids
% C		43 -52	58 -62
% H		3.4 - 5.1	2.9 - 5.4
% N		1.2 - 4.1	3.6 - 4.8
% O		43 -51	29 -32
C:H		10.7 -14.9	10.8 -21.4
C:O		0.8 - 1.2	1.8 - 2.1
COOH	(meq/100 g)	610 -910	150 -300
Phenolic OH	(meq/100 g)	270 -570	290 -570
Alcoholic OH	(meq/100 g)	0 -490	0 -350
C = O	(meq/100 g)	110 -310	90 -300
Optical density 726 to 465 mμ		<0.1 - 0.5	0.1 - 2.5
Weighted average molecular weight		4 000 -7000	50 000 -90 000

*Compiled from Kononova (1966), Manskaya and Drozdova (1968),

Stevenson and Butler (1969) and Orlov *et al.* (1971).

A characteristic of humic substances is their possession of a variety
of functional groups. The most active of these are the carboxyl and
phenolic hydroxyl groups. In addition, alcoholic hydroxyl, carbonyl
methoxy, nitrogen and sulphur containing groups are known to occur.
For a soil humic acid, Wright and Schnitzer (1960) found the following
functional group content (meq/100 g) : carboxyl (180), phenolic
hydroxyl (290), alcoholic hydroxyl (300), carbonyl (300) and methoxy
(50). For a fulvic acid the same authors found: carboxyl (910),
phenolic hydroxide (270), alcoholic hydroxide (490), carbonyl (110)
and methoxy (30). Dubach and Mehta (1963) stated that up to nearly
50% of the oxygen content of humic substances is not accounted for
in functional group analysis and that this is believed to represent
ether , quinone and lactone linkages in the structure. The lower
C:O ratio of fulvic acids compared with humic acids is largely the
result of the former substances having a high content of carboxyl
groups.

1.5 Structure of humic substances

Most discussions of the possible structure of humic substances
are concerned with humic acid. Fuchs (1931) presented a structure,
shown in Figure 1, which was based on his view that unaltered lignin
is an important component.
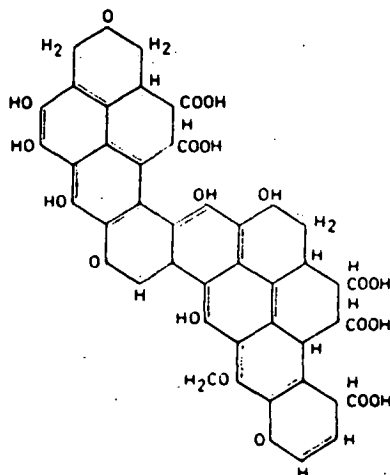
Figure 1. Fuchs (1931) structure of humic acids.

This structure does not allow for the existence of nitrogen compounds and carbohydrates in side chains which has been demonstrated in many studies (e.g. Hobson and Page, 1932; Coulson et al. 1959). As noted earlier, Tyurin (1937) commented that lignin is not essential to the development of humic substances since they develop under lignin deficient grasslands. Finally studies such as those by Adler (1961) have shown that lignin does not have the condensed aromatic structure proposed by Fuchs (1931).

Dragunov et al. (1948) suggested that humic substances have a linear structure in which aromatic units are linked largely through -O-and =N- bridges. This structure, which is shown in Figure 2, provides for both cyclic and side chain nitrogen.
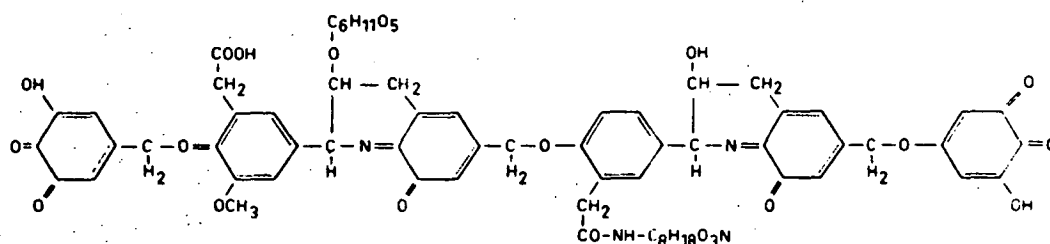
Figure 2. *Dragunov et al. (1948) structure of humic acids.*

This is compatible with the findings of Shmuk (1924) which show that about half the total nitrogen of humic acids passes into solution on acid hydrolysis. It also allows for the presence of carbohydrate chains as found by Coulson et al. (1959) and others. Whilst the structure satisfies many of the restraints of the chemistry of humic substances, carboxyl groups do not feature to the extent their analysed content (Table 1) suggests.

Many other linear structures, similar to those of Dragunov

et al. (1948), have been presented in the extensive literature of

soil science. Murphy and Moore (1960), for example, studied humic

acid extracts from young peat and then attempted to produce synthetic

substances which satisfied both the chemical composition and reactivity

found for the natural products. Their syntheses were based upon

polymerisation of either benzoquinone or catechol and two examples

are shown in Figure 3. These are probably not as complex as the

real structure of humic acids and only allow for phenolic functional

groups.
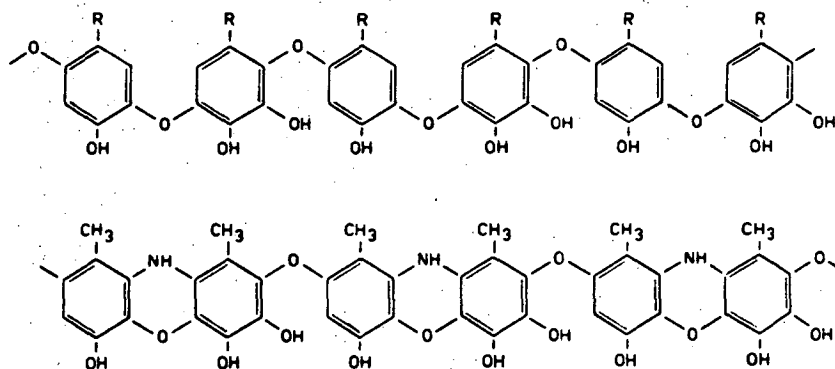
Figure 3. *Murphy and Moore (1960) structures of humic acids.*

Felbeck (1965) also suggested a structure based upon a polymerisation

mechanism and this is shown in Figure 4. This structure also fails

to accommodate the functional groups and side chains known to be

present.
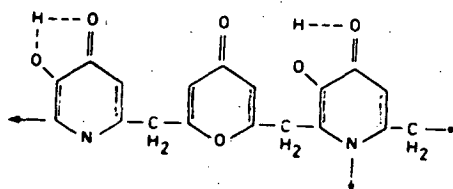
Figure 4. *Felbeck (1965) structure of humic acids.*

There is evidence that the aromatic components are of greater complexity than is indicated by the structures which have been discussed. Cheshire *et al.* (1967) have found compounds such as perylene and coronene amongst the oxidation and destructive distillation products of humic acids. Goodman and Cheshire (1976) have found, by means of electron paramagnetic resonance spectroscopy, evidence for the occurrence of copper porphyrin complexes in humic acids. Nissenbaum and Swaine (1976) comment that humic substances have features in common with macrocyclic compounds. Such entities, examples of which are shown in Figure 5, increase considerably the complexity that a model structure of humic acids must display. In passing it is of interest to note the similarity between pyrene and the structure of Fuchs (1931).

PYRENE   PERYLENE   CORONENE

COPPER PORPHYRIN COMPLEX

EXAMPLE OF MACROCYCLIC COMPOUND
(DIBENZO 8 CROWN 6)
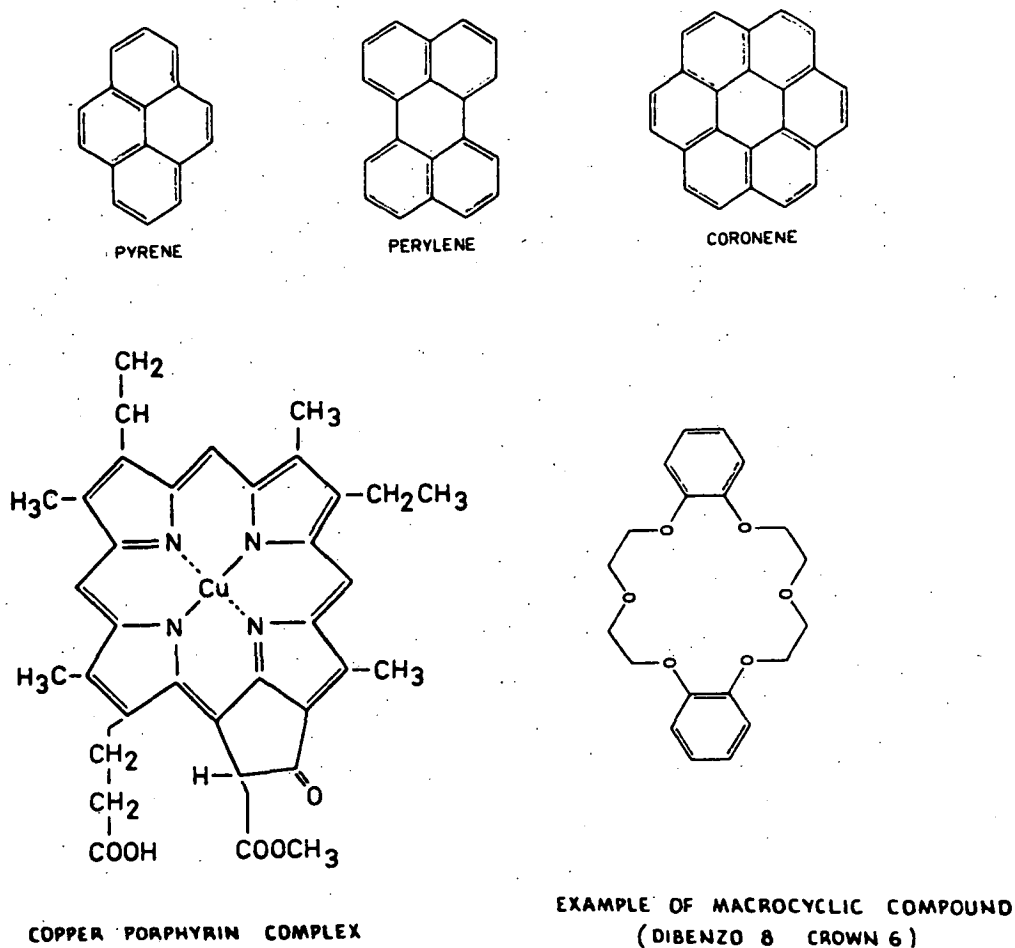
Figure 5. *Examples of complex compounds which may exist in the structure of humic acids.*

Fulvic acids have structural units similar to humic acids,
although they have less strongly expressed aromatic character and a
higher proportion of side chains than the latter group. Kononova
(1966) suggests that fulvic acids may be considered to be the least
mature representatives of humic 12 substances.

1.6 Summary

Humus is generated in the soil during slow decomposition of plant
and animal matter. The humic substances contribute up to 95% of the
composition of humus. On the basis of comment by Kononova (1961, 1966),
Stevenson and Butler (1969) and Flaig et al. (1973), they may be
defined as a group of yellow to black, essentially aromatic substances
of relatively high molecular weight, which ionise to varying degrees
in solution and form complex polyanions. They are dissimilar to the
organic compounds of living organisms, and are the result of poly-
condensation and polymerisation reactions, mainly between phenolic
and nitrogenous compounds produced by bacterial decay and synthesis
in plant and animal residues.

Structurally, the humic substances are extremely complex, and
whilst it may eventually be possible to determine with precision the
contributing units of structure, the highly variable pattern of linkage
of these is likely to be a matter of chance. The comment of Dubach
and Mehta (1963) that possibly no two molecules of humic substances
are the same, may be a little extreme but it highlights the difficulty
of producing a structural scheme to accommodate the complexity of
these substances. Orlov et al. (1971) found the molecules of humic
acid to be of ellipsoidal shape with axial ratios ranging from 1:6
to 1:12. It is thus likely that structures of the type presented
by Dragunov et al. (1948) approach reality, although the character
of the aromatic and other contributing entities is not as simple
as these presentations suggest.

Characteristics of humic substances of importance in considering the interaction with minerals or their weathering products, are the molecular sizes and structures and the functional groups. Since humic substances range to very high molecular sizes, there is no doubt that they will have colloidal properties which may be reflected in their behaviour in the geochemical cycle. The functional groups present, particularly the carboxyl and phenolic hydroxyl, will be of importance in ion exchange and complexation reactions. The present of polyphenol groups, aldehyde groups and carbohydrate residues may influence the capacity of humic substances to act as reducing agents in the geochemical cycle. These possibilities will be examined in subsequent sections of this thesis.

CHAPTER 2

A REVIEW OF THE ACTIVITY OF HUMIC SUBSTANCES IN GEOLOGICAL PROCESSES

2.1 *Early references to the activity of humic substances*

Sprengel (1826) appears to have been the first to note the acidic properties of humic substances and to propose that they attack silicates. Berzelius (1839), Thenard (1870) and Senft (1871, 1874) expressed similar views. In an extensive review of humic substances, Julien (1879), suggested that they were involved in a wide variety of processes including the solubilisation of silica, the formation of bog iron ore and the precipitation of gold in placers.

Clarke (1911) dismissed the claims of the early writers as he found them lacking in experimental evidence. However, the claim by Julien (1879) that humic substances were involved in the solubil- isation of silica was based on the observation that where humus was abundant in the drainage area, there was a high content of dissolved silica in the river water. He found that in the Ottawa River, for example, which drains extensive forests and marshes, silica contributed 33.7% of the total dissolved inorganic solids.

2.2 *The effect of humic substances on silicates*

Many investigations have been made of the action of humic sub- stances on silicates. Guillin (1928) found that feldspar had a higher solubility in solutions of humic acids than in water in contact with atmospheric carbon dioxide. Blanck (1933) maintained that the solubilisation of silicates by solutions of humic acids was due to a high concentration of carbon dioxide produced by their decay. Graham (1941) found that on reaction of humic acids with anorthite, calcium was released to the solution and the pH increased. On the basis of these results he stated that humic acids were effective agents of weathering. Loughnan (1969) has criticised the inter- pretation of increasing pH as evidence for weathering effectiveness. He suggested that the pH change is a hydrolysis effect and the final value in a reaction between silicates and water, will be the abrasion pH values of Stevens and Carron (1948).

From a study of the mineralogy of a podzol soil profile,
Van der Marel (1948) suggested that humic substances were active in
the weathering of silicates. Furthermore, Kononova et al (1964)
exposed pulverised lepidomelane, nepheline, plagioclase and kaolinite
to the action of 0.15% solutions of humic and fulvic acids for ten
days. Maximum activity was displayed by fulvic acids from a sod-
podzolic soil which extracted 1.79 mg Fe_2O_3 and 2.47 mg Al_2O_3 from
lepidomelane and plagioclase respectively. The work of Kononova
et al. (1964) was confirmed in the studies of Ponomareva and
Ragim-Zade (1969), thus allaying the doubt expressed by Krauskopf
(1967) as to the validity of claims for the activity of humic
substances in geological processes.

2.3 The interaction of humic substances with minerals other than silicates.

The literature on the interaction between humic substances and
minerals other than silicates is not extensive. It has already
been noted that Julien (1879) believed that humic substances were
active in the formation of bog iron ore. More recently Strakhov
(1947) has indicated that mobilisation of iron by humic substances
is an important factor in the genesis of these deposits. Experimental
evidence supporting such views was presented by Gruner (1922), who
exposed various minerals to the action of water drawn through a bed
of peat. After 182 days, solutions in contact with magnetite,
siderite and pyrite were respectively found to contain 41, 48 and
14 µg Fe/ml, compared with a blank value of 2 µg Fe/ml.

Harden and Bateson (1963) considered that the action of humic
substances has been a contributing factor in the genesis of the
bauxites of British Guiana. They propose that these substances are
active in leaching silica and iron from kaolinitic clays to form
the bauxite. In addition, Lancho et al. (1976) have proposed that
the formation of fulvic acid complexes with aluminium is responsible

for the development of bauxite over granitic rocks of central
eastern Spain.

Following up his 1934 studies which showed gold to be insoluble,
Fetzer (1946) made a more comprehensive investigation of the solubility
of minerals in humic acids. In addition to repeating his study of
gold, he examined the solubility of a number of sulphide minerals,
and their oxidation products, in humic acids. Precipitated copper
sulphides and oxides were also exposed to the action of humic acids
and a wide variety of simple organic acids. From these studies
Fetzer (1946) concluded that humic acids were no more effective
solvents of minerals than the water in which they were dispersed.

2.4 The action of humic substances on gold

The suggestion by Julien (1879) that humic substances are
involved in the precipitation of gold in placers is worthy of
further consideration. Many geologists concerned with alluvial
gold deposits have observed composite nuggets of gold and organic
matter. The writer has observed these from the Jane River and Lisle
alluvial gold deposits in Tasmania. Friese (1931) examined the
accumulation of gold in a number of Brazilian placer deposits, which
were alleged to have exhibited regeneration of gold about 20 years
after their initial exhaustion. He suggested that the regeneration
was due to the introduction of gold in solutions of humic acids, and
presented experimental evidence of the ability of such solutions to
dissolve this metal. A maximum of 175 mg Au was reported taken into
solution after exposure of 0.005 mm to 0.1 mm gold dust to a 4%
solution of humic acids for 300 hours. Fetzer (1934) attempted to
repeat the experiments of Friese (1931) without success and came
to the conclusion that the gold was not soluble in humic acids.

Shcherbina (1956) and Steelink (1963) accept the solution of gold

by humic acids whereas Ong and Swanson (1969) have found no evidence

for this process.

2.5 The role of humic substances as absorbents of ions from solution

The absorbent role of humic substances is a far less contentious

one than the role of mineral solvent. Rodzyenko (1892) published

the earliest experimental evidence for the absorption of a number

of salts by humin. Lovering (1927) suggested that the accumulation

of native copper in a bog in Montana, U.S.A. was initiated by the

absorption of Cu^{+2} by the organic matter.

The accumulation of metals in peat deposits provides a mechanism

for the enrichment of trace elements in the vitrain of coal, which

is formed from the humic substances of peat. One of the classicial

geochemical studies was that of Goldschmidt (1930) who found

germanium to range up to 11 000 μg/g in the ash of coals. Armands

and Landergren (1960) found up to 900 μg/g of uranium in peat deposits

of Sweden. Szalay (1964) reported that a number of polyvalent cations

including UO_2^{+2} were enriched in peat by factors up to 10 000 times

the values found in associated waters. In later studies Szalay and

Szilagyi (1967) found enrichment of vanadium in peat of the order of

50 000 times the content of associated water. Manskaya and Drozdova

(1968) used selective extraction of uranium from peat to demonstrate

that 95.6% of the metal was present as uranyl humates and fulvates.

Radtke and Scheiner (1970) proposed that the concentration of gold

in the Carlin, Nevada, U.S.A. deposits was in part due to the

absorption of gold complexes from hydrothermal solution by organic

matter similar to humic acids.

2.6 *Mechanisms of the interaction between humic acids and cations*

The uncertain character of humic acids has resulted in a number of interpretations being placed upon their reactions in the geochemical cycle. Originally, Sprengel (1826) regarded the association of humic acid and cations to be the result of simple salt formation. Tarkhov (1881) drew attention to the fact that many associations of humic acids with cations appeared to be non-stoichiometric. The work of Graham in 1861, had brought to light the unusual properties of the colloidal state and interpretations of humic acid activity were sought in this field. Thus Tarkhov (1881) believed that the associations of humic acids and cations could be interpreted as colloidal absorption phenomena. This became the general approach in soil science and Baumann and Gully (1910) applied the absorption model widely in the explanation of many of the properties of humic acids. In the geological field, recent contributions by Ong and Bisque (1968) and Ong *et al.* (1970) have stressed the colloidal activity of humic acids.

Largely as a result of the pioneering work on metal complexation by Fisher (1925, 1937), soil scientists began to look at humic acids as possible complexing agents. The fact that humic acids possess a high content of functional groups suggests that they should be capable of forming metal complexes. This explanation of the association of humic acids with cations has been advanced by a number of investigators including Bremmer *et al.* (1946), Swindale and Jackson (1956) and Wright and Schnitzer (1963).

Humic acid has also been considered to be reducing agent by Garrels and Pommer (1959) in the concentration of uranium through reduction of the uranyl ion UO_2^{+2}. Szalay and Szilagyi (1967) have proposed that humic acids reduce the meta-vanadate ion VO_3^- to the vanadyl cation VO^{+2}, allowing subsequent reaction to form vanadyl humates. Ong and Swanson (1969) also proposed that the reducing properties of humic acids are a feature which influences the transport

of gold. Szalay (1964) has indicated that the mechanism of inter-
action between humic acids and cations can be interpreted as
reversible ion exchange and Bunzl (1974) has made a detailed study
of such exchange reactions.

2.7 Summary

The above review indicates that field observations and experi-
mental studies strongly favour the destruction of silicates either
by humic substances or, as Blanck (1933) suggested, high carbon
dioxide concentrations associated with their decay. The evidence
with respect to the non-silicate minerals is both scarce and
contradictory. It is the aim of this thesis to present further
data and discussion on the activity of humic acids in mineral
degradation. A number of procedures have been applied to gain an
insight into the type of association between humic acids and cations
and these are reported in later chapters. Gold is of particular
interest to the writer, and in view of the fact that its interaction
with humic acids has been a subject of long standing controversy a
chapter is devoted to this problem.

CHAPTER 3

THE HUMIC SUBSTANCES OF SOME NORTH-WESTERN AND WESTERN TASMANIAN SOILS

According to Stephens (1951), the soils of Tasmania are largely podzolic. In later studies Stephens (1961) classified these podzolic soils as podzols, grey-brown podzolic soils, ground water podzols and swamp soils. For this study, sites were selected where examples of these soils were of residual origin, and were developed on predominantly quartzose bedrock. As a result, the soils were of sandy character with no marked profile development. They generally consisted of grey to brownish humic sands with widely variable contents of organic matter. The sample locations, soil type, vegetation type and organic matter content are given in Table 2. In the following sections the procedures used to extract and study the humic substances of the selected soils are described.

3.1 Soil sampling and preparation

The soils were sampled by excavating a 1 m by 0.5 m pit to bedrock and taking a bulk sample of the humic sands over the total vertical exposure, exclusive of the A_0 (litter) horizon. The bulk samples were oven dried at 40°C, disaggregated by hand crushing in a mortar, and sieved through a 1 mm mesh nylon sifting cloth to remove roots and fibres.

3.2 Determination of total organic matter content

The total organic matter in a soil free of hydrated silicates and carbonates can be determined by a simple ashing procedure. After air drying at 110°C for ten hours, 10 g samples were ashed at 800°C for one hour and the organic matter content measured by the weight loss.

3.3 Extraction and estimation of the content of humic substances

A number of chemical procedures have been developed for the extraction of humic substances. Depending on the soil type, it may be necessary to pretreat the soil so that associations of mineral

Table 2. *LOCATION DATA, SOIL TYPE, VEGETATION COVER AND ORGANIC MATTER CONTENT FOR SOME TASMANIAN SOILS*

Sample	Location*	Soil type	Predominant vegetation/ type	Organic matter content %
TS-1	Oliver Hill [DP295035]	Podzol	White topped stringybark *(Eucalyptus delegatensis)*	
			Bracken fern *(Pteridium aquilinum)*	2.4
TS-2	Machinery Creek [DP303045]	Swamp soil	Moss *(Sphagnum spp.)*	17.7
TS-3	Mt Roland [DQ403120]	Podzol	Tea tree *(Melaleuca ericifolia)*	12.8
TS-4	Savage River [CP418037]	Groundwater Podzol	Button grass *(Gymnoschoenus sphaerocephalus)*	26.2
TS-5	Paradise [DQ436090]	Grey-brown podzol	Radiata pine *(Pinus radiata)*	27.4

*Universal grid reference. 1:100 000 Tasmanian topographic map series.

matter with the humic substances will be broken down, before attempting extraction of the latter. Dubach et al. (1964) have investigated the most commonly applied procedures. Since the organic matter of podzolic soils developed over quartzose bedrock does not have strong links with soil minerals, a relatively simple extraction procedure may be used.

The method used in this study is essentially that developed by Kononova and Bel'chikova (1960). In detail, the procedure was as follows: 50 g samples of the minus 1 mm soil were mixed with 200 ml 1:1 $C_2H_5OH-CHCl_3$ in bottles sealed with air tight caps. These were transferred to an oven at 60°C and shaken intermittently for four hours. After this treatment the soils were filtered in a Büchner arrangement and washed with a further 100 ml of $C_2H_5OH-CHCl_3$. The soils were dried to remove traces of the organic solvents, returned to the bottles and mixed with 500 ml of an aqueous solution of 0.1 M $NaOH$-0.1 M $Na_2P_4O_7$. Dubach et al. (1964) have commented that alkaline extraction is likely to increase the degree of oxidation of humic substances, and also results in a product of lower molecular weight than is the case in the parent sample. These changes can be minimised by carrying out the extraction under nitrogen, and this gas was used to sweep air out of the bottles before they were sealed and shaken intermittently over a 24 hour period.

After the period of agitation the bottles were left for two hours to allow the solids to settle. The solutions were then decanted through 0.10 mm (200#) nylon sieve cloth into beakers and stirred with an $-SO_3H$ type cation exchange resin (Amberlite IR-120) in the H^+ form. A resin grain size of 0.35 mm to 0.20 mm (50# to 100#) was used to facilitate separation of the resin beads from the soil extracts which contained clay size mineral particles. The solutions were stirred continuously until the excess alkalinity had been neutralised at about pH = 7. The soil residues were shaken with

200 ml portions of distilled H_2O and after settling the washings were added to the original extracts. This procedure was repeated several times to remove traces of soluble organic matter from the soils. The soil residues were retained for estimation of the humin content.

When the soil extracts had a pH of about 7, they were filtered through the 0.10 mm sieve cloth to separate the resin beads, and then passed through a Sharples supercentrifuge at 25 000 rpm to remove the clay-size mineral particles. The solids from this operation were added to the soil residue. The organic matter extracts were purified by ion exchange treatment as suggested by Hori and Okuda (1961). This involved passing the solutions through ion exchange columns of Amberlite IR-120 (cation) and IRA-400 (anion) to remove excess salts and convert the humic substances to the H^+ form.

At this stage of the extraction there were two fractions, which were the soil residues with humin and solutions containing humic acids, fulvic acids and the individual organic compounds. The soil residues were dried at 110°C as in the case of the original soil and ashed at 800°C to estimate the humin content. The solutions were adjusted to pH = 2 with H_2SO_4 which precipitated humic acids. These were separated by use of the supercentrifuge. The humic acid samples were taken into solution with 0.1 M NaOH and immediately batch treated with ion exchange resins IR-120 and IRA-400 to return them to the H^+ form. They were then dried in an oven at 40°C and weighed. The solutions from the supercentrifuge contained the fulvic acids and the individual organic compounds. These were treated with the ion exchange resin IRA-400 to remove sulphate, dried at 40°C and weighed. The preparation of stocks of humic acids for the experimental studies described in this thesis, followed the procedures described above, scaled up to accommodate 1 kg soil samples. The extraction

and fractionation scheme is summarised diagrammatically in Figure 6.

3.4 Fractions of humic substances in the Tasmanian soils

The humic substances of the selected Tasmanian soils were extracted and fractionated by the procedures described in 3.3. The results, which are given in Table 3, show that the humin fraction is high in all soils, ranging from 20% to 80%. These figures are unlikely to reflect the true humin content of the soils, since the quantity of alkali insoluble organic matter is masked by the presence of large amounts of charcoal resulting from the frequent bushfires to which the localities have been subjected. If the values for humin are excluded on the basis that this component should be low in a podzolic soil over quartzose bedrock, then 80% to 95% of the organic matter of the soils is humic acids. Only the swamp soil (TS2) and the grey-brown podzol (TS5) have a significant proportion of fulvic acids and individual organic compounds. The ash content of the extracts of humic acids ranged from 2.5% in THA-1 to 23.4% in THA-5. Treatment of the samples with 40% HF for one hour at 60°C as proposed by Brown *et al.* (1959) reduced the ash contents of all but THA-5 to less than 2%.

Table 3. HUMIC SUBSTANCES IN THE TOTAL ORGANIC MATTER OF SOME TASMANIAN SOILS

Sample	Humin	Humic acid %	Fulvic acid and individual compounds (%)
TS-1	25.2	74.2	0.2
TS-2	19.8	73.1	6.3
TS-3	70.3	27.9	0.7
TS-4	79.4	19.3	0.8
TS-5	69.7	24.8	5.0

Minus 1 mm soil sample

Extraction with 1:1
CHCl$_3$ - C$_2$H$_5$OH

Filter

Residue → Humic substances
Individual organic
compounds
Mineral components

Solution - fats
and waxes

Shake 24 hr with 0.1 M NaOH-
0.1 M Na$_4$P$_2$O$_7$ under nitrogen

Allow to settle, decant solution and wash
soil with water until washings are clear.

Run total solution through supercentrifuge

Residue - Humin and
mineral components

Solution → Humic acids
Fulvic acids
Individual organic
compounds

Adjust pH to 2.0 with H$_2$SO$_4$

Supercentrifuge

Residue - Humic
acids

Solution - Fulvic acids and
individual organic compounds

Treat with IR-120 and
IRA-400 to remove
excess salts convert
humic acids to H-form

Treat with 40% HF to
remove trace silicates

Figure 6. *Extraction and fractionation scheme for humic substances.*

3.5 Composition of the humic acids

Analytical data for the humic acids were provided by the CSIRO Microanalytical Service, Melbourne, Australia. An optical study was made of 20 $\mu g/ml$ aqueous solutions of the samples after the method of Welte (1955) in which the absorbance at 472 nm (E_4) and 664 nm (E_6) is compared. These data are given in Table 4 which also includes for comparison, values for a Russian chernozem and podzol.

The humic acids from Tasmanian podzolic soils differ from that of a typical Russian podzol. The nitrogen contents of the Tasmanian samples are generally lower whilst there is a higher proportion of oxygen. Until more information is available on the nature of the organic matter of soils developed in wet temperate regions under indigenous Australian floras, the reasons for these variations will remain conjectural. Some chemical entities, which are ultimately included in the humic acid structure, may vary in type and amount according to the predominant plant species from which they originate. Thus the residues of eucalypts, for example, may differ in composition from those of a pine forest. The low nitrogen values of the Tasmanian samples of humic acids may be the result of the removal of hydrolysable nitrogen-containing components by the extraction and ash reduction procedures.

Of the Tasmanian samples, only THA-5 approaches the characteristics of a podzol humic acid. The soil from which this sample was extracted was developed under a forest of imported conifers which were set out about forty years ago. On the basis of the limited chemical and optical data the other samples, although extracted from podzolic soils, show an affinity with either chernozems or an intermediate between chernozems and podzols.

Table 4. *COMPOSITIONAL AND OPTICAL DATA FOR HUMIC ACIDS FROM TASMANIAN SOILS*

Sample	*C %	H %	N %	O %	C:H	C:O	Optical data E₄ : E₆ (472 nm) (664 nm)
THA-1	59.9	2.9	1.9	34.1	20.3	1.8	2.9
THA-2	56.8	3.6	2.4	37.0	20.5	1.5	3.0
THA-3	54.0	4.0	3.3	38.4	13.5	1.4	3.6
THA-4	55.5	4.2	3.6	36.6	13.2	1.5	3.8
THA-5	52.8	4.7	3.2	38.9	11.2	1.4	4.2
Northern podzol Arkhangel region	58.1	5.4	4.5	32.0	10.8	1.8	ca 5.0
Ordinary chernozem Voronezh region	62.1	2.9	3.6	31.4	21.4	2.0	ca 3.5
(Kononova, 1966)							

*Composition given on an ash-free basis from analyses by CSIRO Microanalytical Service, Melbourne, Australia.

More detailed comparisons of the organic matter of the relatively
few soils examined and the soils of other regions are beyond the
scope of this thesis.

3.6 *Nature of humic acids in relation to chemical composition and optical properties*

Kononova (1966) suggested that the C:H ratios for humic acids
may be used as an indication of their degree of aromatisation.
From the values given in Table 4 this property increases in the
order THA-1 = THA-2 >THA-3 = THA-4 >THA-5. Welte (1955) has
demonstrated that an indication of the distribution of carbon
between an aromatic network and aliphatic side chains is reflected
in the absorbance ratio $E_4:E_6$. The lower the $E_4:E_6$ ratio the
greater the degree of condensation to aromatic structures. For the
Tasmanian samples of humic acids it is apparent from Table 4 that
the absorbance ratio $E_4:E_6$ are consistent with the C:H ratios.

The relative proportions of aromatic units with hydrophobic
properties and aliphatic units with hydrophylic properties in the
structure of humic acids determines their mobility. On this basis
the mobility of the Tasmanian samples of humic acids could be
expected to increase from THA-1 to THA-5. This may be demonstrated
experimentally by use of paper chromatography with 0.04 M $Na_2B_4O_7$
as solvent. The result for THA-1 and THA-5 which have extremes
of C:H ratio and absorbance ratio, is shown in Figure 7. It can
be seen that this indicates that THA-5, which on the basis of C:H
ratios and optical properties is more hydrophylic than THA-1, is
in fact more mobile. Since both samples display considerable
movement however, the difference in mobility is not likely to be of
significance in geological processes.
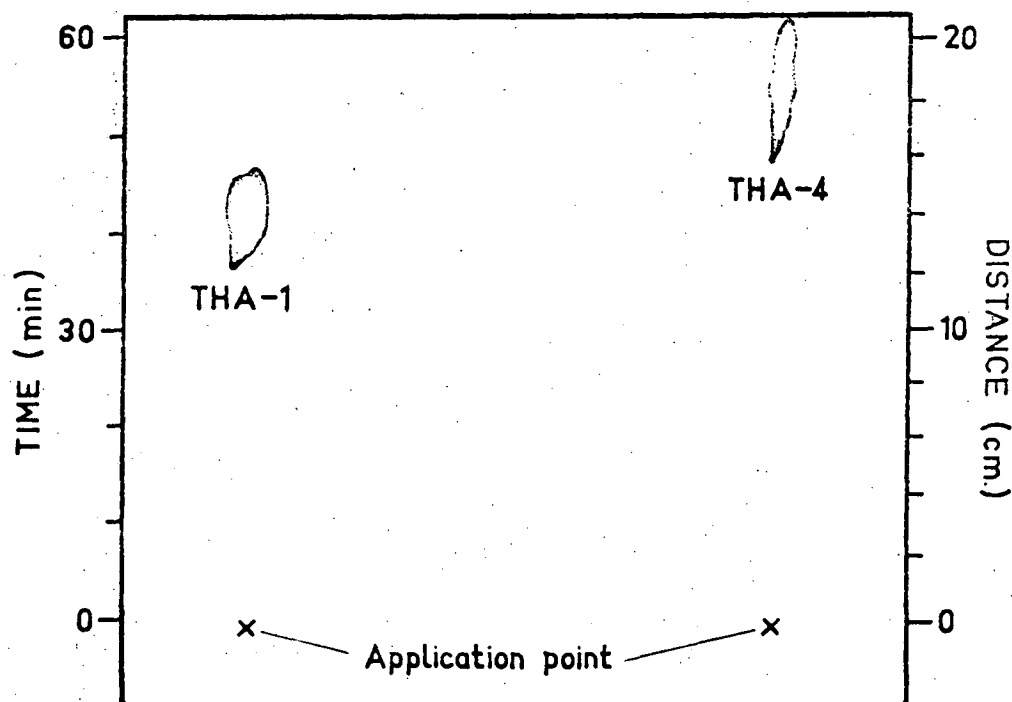
Figure 7. *Paper chromatogram of humic acids THA-1 and THA-5 with 0.04 M Na$_2$B$_4$O$_7$.*

3.7 Infra-red spectra of the humic acids

Infra-red spectra were recorded from humic acids THA-1, THA-2, THA-3, THA-4 and THA-5 over the frequency range of 4000 to 600 cm^{-1}, using a Beckman IR-9 instrument. The samples were prepared for study by mixing thoroughly dried humic acids and KBr in the proportion 1:400 and pelletising. The spectra were recorded against a blank of KBr and are shown in Figure 8.

The spectra are very similar to one another and show the broad absorption characteristics of humic acids. According to the summary by Flaig et al. (1975), the absorption bands recognisable in Figure 8 may be assigned to:

3450-3300 cm^{-1}	Hydrogen bonded OH groups, free OH, intermolecular bonded OH.
2950-3850 cm^{-1}	Aliphatic C-H, C-H$_2$ and C-H$_3$ stretching.
1725-1640 cm^{-1}	C = O stretching of carboxylic acids, cyclic and acyclic aldehydes and ketones, quinones.

1640-1585 cm^{-1}	C = C stretching vibration of double bonds in cyclic and acyclic compounds, benzene rings, substitution.
1470-1420 cm^{-1}	Aliphatic C-H deformation.
1280-1137 cm^{-1}	C-O stretching of esters, ethers and phenols.

The band due to aliphatic stretching (2950-2850 cm^{-1}) is seen to be more pronounced for THA-3, THA-4 and THA-5 which is consistent with the compositional and optical data given in Table 4.

3.8 Trace element content of the humic acids

Since the Tasmanian samples were extracted with a view to studying their effectiveness in mineral degradation, it was essential to have knowledge of their trace element composition. All trace element analyses reported in this thesis were carried out by atomic absorption spectrophotometry (AAS) using a Varian-Techtron AA4 instrument. In the case of the humic acids, analyses were made of solutions prepared by dissolving 0.5 g samples in 100 ml of 5% ammoniacal EDTA. The results, which are given in Table 5, showed that except for THA-5 the trace element content was low. The high iron and silicon content of THA-5 explains the high ash figure obtained in the analysis of this sample of humic acids.

The sodium content of the samples was relatively high and this may be related to the use of NaOH-Na$_2$P$_4$O$_7$ in the extraction procedures. If, as suggested by Nissenbaum and Swaine (1976), humic acids behave as macrocyclic compounds, then sodium might be retained by being fixed in protected sites in the structure.
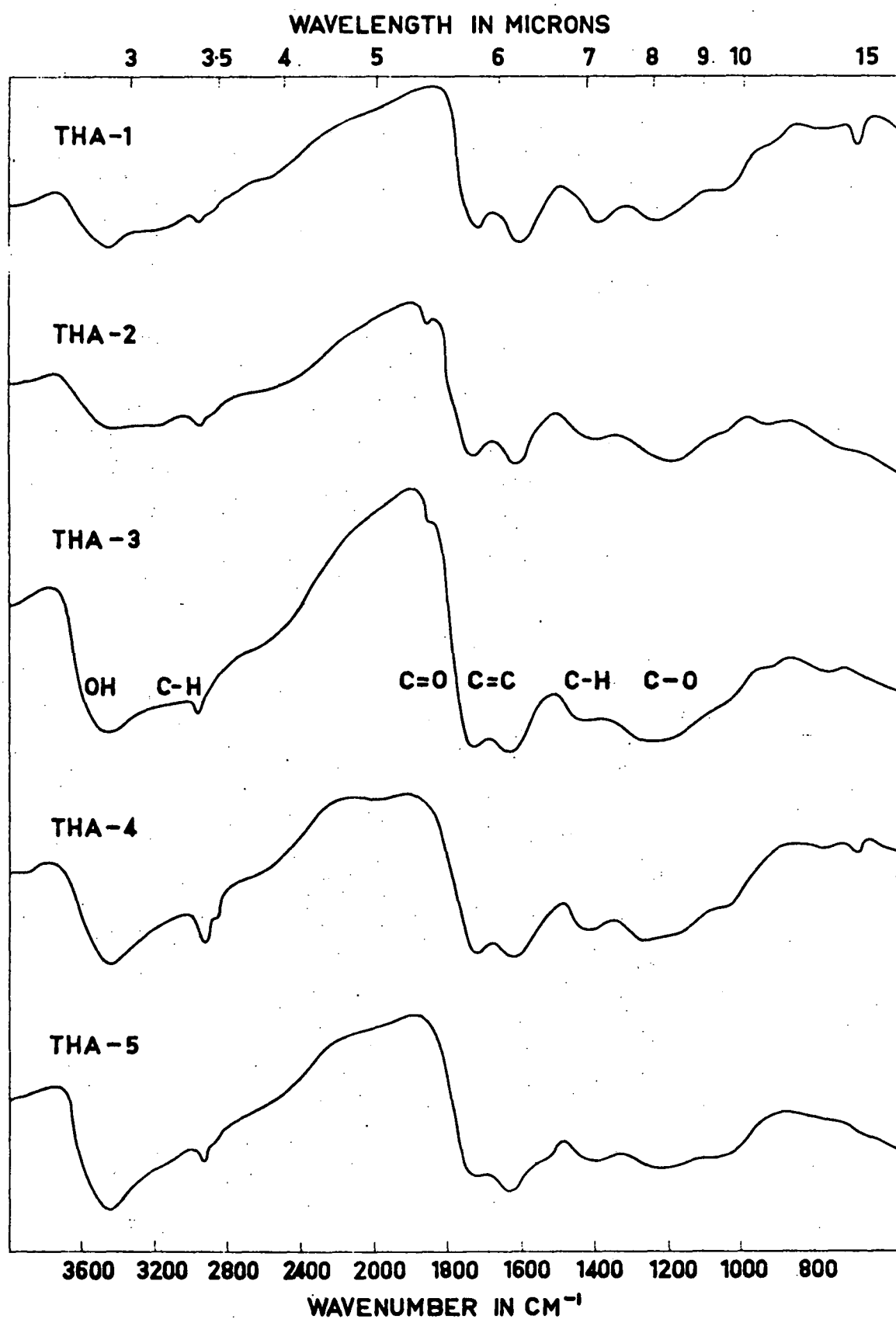
Figure 8. *Infra-red spectra of Tasmanian samples of humic acids.*

Table 5. *TRACE ELEMENT CONTENT OF TASMANIAN HUMIC ACIDS (mg/g)*

| Element | Humic acid sample | | | | |
	THA-1	THA-2	THA-3	THA-4	THA-5
Ca	0.3	0.9	1.2	1.2	0.7
Fe	4.0	1.8	4.7	1.2	26.4
Mg	0.1	0.1	0.1	0.1	0.3
Na	4.0	7.8	9.5	4.0	4.8
K	0.2	0.3	0.2	0.2	0.4
Al	4.0	2.0	4.0	<1.0	14.0
Si	<5.0	<0.2	<0.2	<0.2	<0.2
Mn, Ni, Co, Cu, Zn, Pb, Ba, Sb, Bi	<0.2	<0.2	<0.2	<0.2	<0.2

*Range for these elements   <0.01-0.18

CHAPTER 4

EXPERIMENTAL STUDIES OF THE SOLVENT ACTIVITY OF HUMIC ACIDS

The literature review in Chapter 2 indicates that, despite some comment to the contrary, experimental evidence favours solution of silicates by humic acids. In the case of non-silicate minerals and metals there is very little information available. It is thus desirable that the role of humic acids as solvents of these materials be critically evaluated, and comparisons made with the activity of simple organic compounds and CO_2 enriched waters.

4.1 Constraints on experimental design

In the study by Fetzer (1946), polished mineral surfaces, pulverised minerals and chemical precipitates were used in association with aqueous preparations of humic acids up to strengths of 2.5% (w/v). Whilst such studies may provide useful information, the experimental conditions are far removed from those existing in nature.

In order to design procedures which are compatible with the natural environment, the type of weathering conditions must be taken into account. Under wet cool temperature conditions, weathering of minerals takes place at an irregular interface between soil and rock, where the constituents of the soil water react with solid mineral surfaces. The content of humic substances in soil water is not well known but for the purposes of this study it is only necessary to set a reasonable upper limit. Spectrophotometric determination of the concentration of humic substances in creek and river waters draining button grass plains in western Tasmania, by the method of Welte (1956), has yielded values in the range of 5 mg/*l* to 40 mg/*l*. Such waters are very much diluted by direct run-off and it would be reasonable to expect the concentration of humic substances in soil water of these areas to exceed the drainage water values by a factor of at least ten. Support for this view was found in a seepage sample collected from a tunnel in the Gordon River hydro-

electric power development scheme which was found to contain 430

mg/*l* of humic substances. This level of concentration also compares

favourably with values of up to 300 mg/*l* given by Fotiyev (1971)

for marsh waters of the U.S.S.R. On the basis of this information

it was decided to make use of concentrations of 500 mg/*l* humic acids

for the experimental studies.

The use of pulverised mineral samples, as has been the case in

most previous studies, results in the exposure of large surface areas

to potential solvents and this is likely to substantially increase

reaction rates. In order to reduce this surface area effect, samples

used in the following studies were sieved to a grain size range of

0.30 mm to 0.60 mm (50# to 30#). Simulation of the seepage of water

over fractured surfaces at the interface between soil and rock was

attempted with the experimental arrangement shown in Figure 9.

The solid sample was contained in a glass tube sealed at one end with

0.10 mm mesh (140#) nylon sieve cloth. This tube was suspended in a
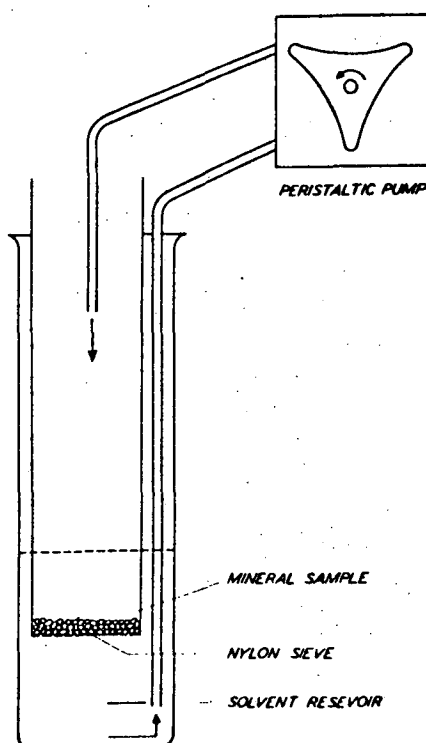
Figure 9. *Experimental arrangement for study of the interaction
between humic acids and minerals under normal
atmospheric conditions.*

reservoir containing 50 ml of the solvent under study and slow circulation through the sample bed was maintained by use of a peristaltic pump. Although surface areas vary considerably according to the manner in which samples crush, an attempt was made to keep this factor constant by taking a mass in grams equal to the specific gravity of each of the samples studied.

The normal exposure time of the samples to the action of potential solvents was 24 hours, although differences in reactivity of samples required some variation in the duration of experiments. The activity of the various solvents was measured by analysis for a key metal in solution by means of AAS. The results were corrected where necessary for the trace element content of the solvents. Some information concerning silicates, precipitated sulphides and pulverised minerals is included in this chapter. This has been taken from the results of preliminary studies of the activity of a 1 g/l solution of THA-1 (Baker, 1973).

4.2 The action of humic acids on some minerals of economic deposits

A group of sulphide, oxide, secondary and carbonate minerals found associated with economic deposits, initially crushed and sieved to a grain size range of 0.30 mm to 0.60 mm, were exposed to the action of 500 mg/l solutions of THA-1, THA-2, THA-3, THA-4 and THA-5 under the conditions described in section 4.1. The average analytical results for duplicate runs are given in Table 6. The complete analytical data are given Appendix 1, Tables 1-6. The variation between duplicate results ranged from about 10% to 40%. The magnitude of this variation is not surprising in view of the dynamic nature of the experiments, the uncertainty of surface areas and the difficulty experienced in completely recovering reaction products from the sample layer prior to analysis.

Table 6. REACTION OF MINERALS WITH H_2O/ATMOS. CO_2 AND 500 mg/l SOLUTIONS OF HUMIC ACIDS

Mineral	Composition	Element determined	μg/ml* in solution after 24 hours extraction by:					
			H_2O/atmos. CO_2	THA-1	THA-2	THA-3	THA-4	THA-5
Galena	PbS	Pb	1.1	50	30	7.8	25	19.1
Bornite	Cu_5FeS_4	Cu	2.0	25	19.6	20	25	25
Sphalerite	ZnS	Zn	1.6	2.6	2.1	2.3	1.9	1.9
Pyrite	FeS_2	Fe	0.9	4.7	11.9	2.4	1.9	7.2
Loellingite	$FeAs_2$	Fe	1.1	100	60	25	25	40
Bismuthinite	Bi_2S_3	Bi	0.7	40	50	20	40	40
Stibnite	Sb_2S_3	Sb	0.3	2.8	9.6	1.4	3.9	0.7
Hematite	Fe_2O_3	Fe	1.1	11.6	3.8	1.6	1.8	6.7
Magnetite	Fe_3O_4	Fe	2.0	10.7	20	2.7	6.7	7.4
Pyrolusite	MnO_2	Mn	3.3	30	15.5	11.4	25	11.6
Azurite†	$Cu_3(OH)_2(CO_3)_2$	Cu	4.2	440	240	210	290	160
Anglesite†	$PbSO_4$	Pb	3.0	1110	510	1100	590	340
Calcite†	$CaCO_3$	Ca	13.0	350	230	220	250	210
Magnesite	$MgCO_3$	Mg	4.3	20	18.6	8.6	17.8	11.2

*Values above 20 μg/ml and 100 μg/ml rounded to nearest 5 and 10 respectively.

†Metal in solution calculated from 3 hour run.

The values for metal extracted indicate that the humic acids

are strong solvents of minerals, since the 500 mg/l solutions

are far more aggressive than is water in equilibrium with atmospheric

carbon dioxide (H_2O/atmos. CO_2). For the sulphides, the extraction

of metals from the minerals by the humic acids varies over a range

of 0.7 µg Sb/ml from stibnite to 50 µg Pb/ml from galena. These

are to be compared with values of 0.3 µg Sb/ml and 1.1 µg Pb/ml

for the extraction by H_2O/atmos. CO_2. For the oxides, pyrolusite

is generally more affected than the iron oxides, with a maximum of

30 µg Mn/ml being released. Anglesite is the most vulnerable of

the secondary minerals, yielding 1110 µg Pb/ml. Of the humic acid

samples studied, THA-1 which developed in soil under an abundant

cover of bracken fern (*Pteridium aquilinum*), appears to be the most

aggressive. This is compatible with the view expressed by Birrell

et al. (1970) that humic acids derived from this plant may accelerate

soil profile development.

The results of the interaction of the 1 g/l THA-1 solution with

precipitated sulphides and pulverised minerals are given in Table 7.

These were obtained by circulating 20 ml of the humic acid solution

for 30 minutes through the fine-grained samples, which were retained

on a macerated filter paper pad in a Büchner funnel. The data are

seen to be largely compatible with those obtained for the coarse-

grained samples (Table 6). Some differences, such as the closer

extraction values for pyrolusite and hematite are apparent and

discussion of these will be undertaken in the next section.

Table 7. REACTION OF PRECIPITATED SULPHIDES AND PULVERISED MINERALS WITH H_2O/ATMOS. CO_2 AND A 1 g/l SOLUTION OF THA-1.

Sample	Element determined	μg/ml* metal in solution after 30 minutes extraction with:	
		H_2O/atmos. CO_2	1 g/l THA-1
Lead sulphide	Pb	<0.2	105
Zinc sulphide	Zn	3.8	4.8
Cupric sulphide	Cu	<0.1	25
Nickel sulphide	Ni	20	70
Bismuth sulphide	Bi	<0.3	3.5
Antimony sulphide	Sb	<0.3	<0.3
Bismuthinite	Bi	<0.3	20
Stibnite	Sb	<0.3	1.2
Hematite	Fe	<0.3	17
Pyrolusite	Mn	0.3	15.5

*Values above 20 μg/ml and 100 μg/ml rounded to nearest 5 and 10 respectively.

4.3 Interpretation of the interaction of humic acids and minerals

As was noted in section 2.6 the interaction between humic acids and the metallic elements has been explained with the humic acids acting as simple acids, colloids, complexing agents or ion exchangers. The vigorous activity of solutions of humic acids towards minerals, which is evident in the extraction values of Table 6, is most readily explained by assigning a complexing role to the humic acids. A detailed analysis of such a possible role is extremely difficult, due to the fact that the abundant functional groups of humic acids occur as structurally indeterminate arrays. This is likely to lead to variable stability of the metal complexes with different samples and may also result in selective complexing properties. Further discussion of this matter will be undertaken in Chapter 7 which deals with miscellaneous approaches to the problems of the interaction between cations and humic acids.

In the natural environment, the wide variability in crystallisation of minerals results in the development of surfaces of differing character and reactivity. This is illustrated by the solubility data for hematite and pyrolusite in THA-1 (tables 6, 7). In experiments with the 0.30 mm to 0.60 mm grain size material, pyrolusite (30 µg Mn/ml) had a greater solubility than hematite (11.6 µg Fe/ml). For the pulverised samples the respective amounts of metal entering solution were 15.5 µg Mn/ml and 17 µg Fe/ml. An explanation of this pattern of solubility is to be found in the differing crystallisation of the pyrolusite and hematite samples. The former mineral consisted of a very fine-grained aggregate whilst the latter was coarsely crystalline. As a result, size reduction has the greater effect, through increasing surface area, on the solubility of the hematite.

The bonding energy of minerals is an important factor in their stability, although unfortunately there is considerable uncertainty in the determination of this energy (Nockolds, 1966; Bachinski, 1969). Despite this problem some correlation is evident between the extraction of metals by humic acid and the relative bond strengths of the sulphides involved. Thus the high solubility of galena compared with sphalerite (table 6) is compatible with the relative bonding energies of these minerals as given by Bachinski (1969). In an experiment with coarse-grained samples of the Cu sulphides: chalcopyrite, bornite, covellite and chalcocite, the amounts of copper extracted after 24 hours exposure to a 1 g/l solution of THA-1 were 1.4, 18, 45 and 150 µg Cu/ml respectively. This is also in accordance with the relative stabilities of these minerals as given by Bachinski (1969).

The structural stability of several iron sulphides and arsenides from the ligand field theory approach has been examined by Nickel (1969). The arsenides are of lower stability than the sulphides and this is reflected in the high solubility of loellingite

relative to pyrite (table 6). Although similar studies have not

been made for nickel minerals, it is likely that the relative

structural stability of heazlewoodite (Ni_3S_2), breithauptite

(NiSb) and pararammelsbergite ($NiAs_2$) explains their solubility

in THA-1. These minerals were reacted with a 1 g/ml solution of

THA-1 for 24 hours and this resulted in extractions of nickel from

the sulphide, antimonide and arsenide of 430, 590 and 740 µg/ml

respectively.

Contrary to the sequence of bond strengths given by Nockolds

(1966) is the high solubility of bismuthinite compared with stibnite

(40 µg Bi/ml and 2.8 µg Sb/ml with THA-1 for example). It is not

clear what factor causes the differing behaviour of these structurally

similar minerals, although possibly differences in oxidation

characteristics have some influence. Comparative thermodynamic data

for the formation of Bi^{3+} and Sb^{5+} in solution are not available

although the respective free energies of formation of Bi_2O_3 and

Sb_2O_5 of -4.97×10^5 joule/mole and -8.39×10^5 joule/mole, indicate

that the oxidation of Sb proceeds readily to the 5+ state. In terms

of the concept of ionic potentials of the elements, first applied in

geochemistry by Goldschmidt (1934, 1937) this would cause a marked

separation of bismuth and antimony and could explain their differing

behaviour. This is illustrated on the ionic potential diagram of

Shcherbina (1956) shown in Figure 10, which gives approximate fields

of location of elements which occur as simple cations, complex ions

and various anionic combinations.
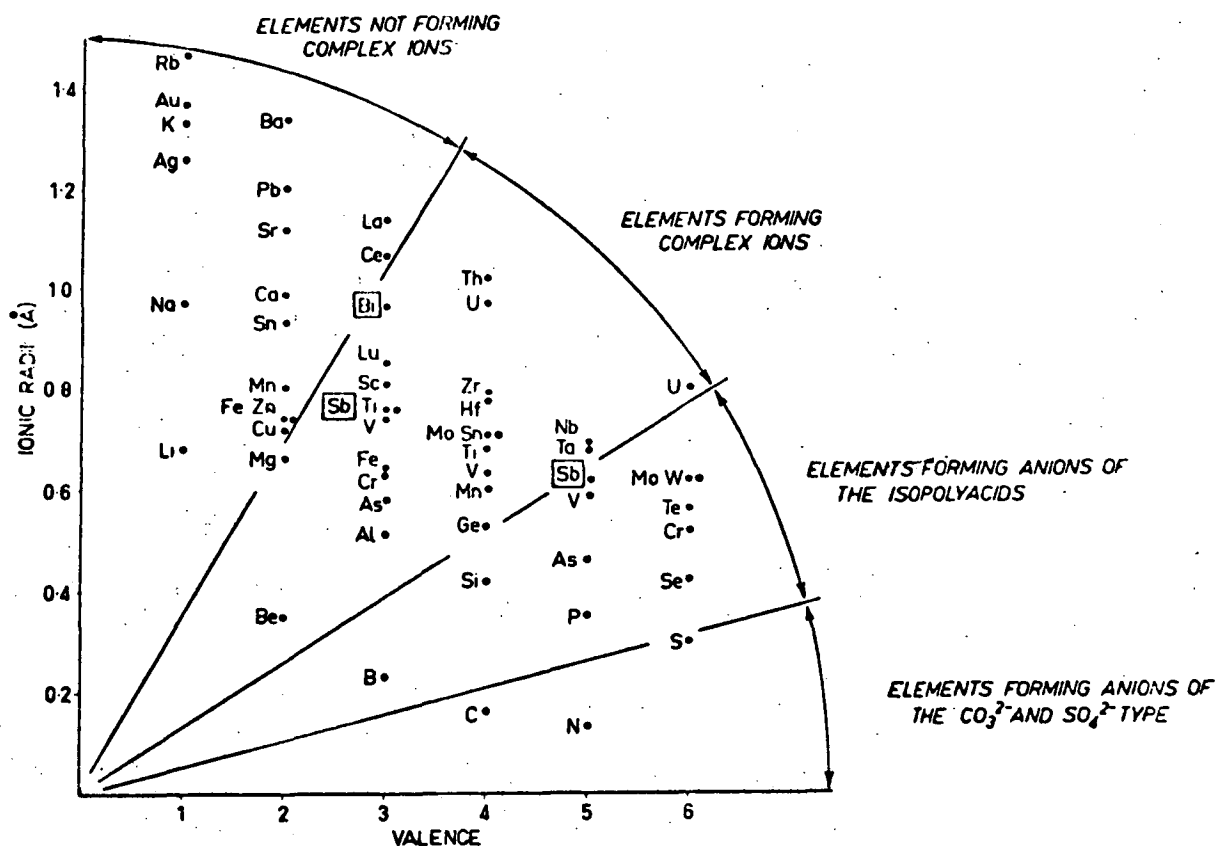
Figure 10. *Ionic potential diagram of the elements (modified after Shcherbina, 1956).*

The activity of humic acids in mineral degradation which is apparent from the results of Table 6 is contrary to the observations of Fetzer (1946). The reason for the difference is not obvious, although it could be due to the fact that in the latter investigations, signs of activity were sought mainly in the etching of polished mineral surfaces. Fetzer (1946) also carried out experiments with precipitated sulphides and reported no solvent activity for humic acids. This is at variance with the results given in Table 7. If all results are scaled to a common basis of metal in solution after 24 hours the following comparison can be made. Fetzer (1946) found that for CuS, a 1% solution of humic acids yielded 1.4 µg Cu/ml whereas the value for H_2O/atmos. CO_2 was 3.4 µg Cu/ml. In the present study the comparable values are 1200 µg Cu/ml for a 1 g/l (0.1%) solution of THA-1 and <5 µg Cu/ml for H_2O/atmos. CO_2. It is possible that the low values obtained in the earlier studies, may have been

due to the fact that the copper released occurred as insoluble humates, which escaped analysis.

4.4 The action of some simple organic compounds on minerals of economic deposits

A wide variety of simple organic compounds occur associated in minor quantities with the humic substances of soils. These include many acids, phenolic compounds and carbohydrates. A number of critics of the role of humic acids in weathering (Murray and Love, 1929; Fetzer, 1946; Krauskopf, 1967) have advanced the view that these simple organic compounds are more likely to be the active substances. To test the validity of this claim, the effectiveness of salicylic acid, citric acid, glycine, alanine, catechin and fructose as solvents of minerals was examined by the procedures used for the samples of humic acids.

The average results of these experiments are given in Table 8, and the complete analytical data are given in Appendix 1, Tables 7-13. The values indicate that, with the exception of the attack on copper minerals by citric acid and glycine, the simple organic compounds are marginally less effective than humic acids. In view of the fact that these compounds seldom provide more than 5% of the total organic reserves of the soil their contribution to weathering, relative to humic acids, must be considered limited. Furthermore, Barber (1968) has drawn attention to the fact that the simple substances do not long survive in the soil since they are rapidly converted to CO_2 by the micro-organisms present.

4.5 A comparison of the effect of humic acid and CO_2 enriched solutions on minerals

It has been claimed by Blanck (1933) that it is the CO_2 generated by decay of humic acids that is the effective weathering agent. This proposition was tested by examining the effectiveness

Table 8. REACTION OF MINERALS WITH H_2O/ATMOS. CO_2 AND 500 mg/ml SOLUTIONS OF SIMPLE ORGANIC ACIDS

Mineral	Composition	Element determined	H_2O/ atmos. CO_2	Salicylic acid	Citric acid	Glycine	Alanine	Catechin	Fructose
Galena	PbS	Pb	1.1	14.6	18.3	1.7	2.1	5.2	1.6
Bornite	Cu_5FeS_4	Cu	2.0	30	60	80	7.2	9.8	2.3
Sphalerite	ZnS	Zn	1.6	1.6	1.4	1.4	1.4	1.6	1.5
Pyrite	FeS_2	Fe	0.9	1.1	1.5	0.9	1.0	1.0	0.8
Loellingite	$FeAs_2$	Fe	1.1	70	60	1.3	1.6	9.0	1.7
Bismuthinite	Bi_2S_3	Bi	0.7	2.5	25	20	13.7	35	8.3
Stibnite	Sb_2S_3	Sb	0.3	0.1	0.3	0.7	0.3	0.9	0.4
Hematite	Fe_2O_3	Fe	1.1	1.5	1.6	1.1	1.5	1.4	1.2
Magnetite	Fe_3O_4	Fe	2.0	9.1	35	2.0	2.1	3.5	2.3
Pyrolusite	MnO_2	Mn	3.3	60	50	7.5	3.6	8.2	5.3
Azurite†	$Cu_3(OH)_2(CO_3)_2$	Cu	4.2	580	1520	800	140	190	5.0
Anglesite†	$PbSO_4$	Pb	3.0	270	480	180	190	230	140
Calcite†	$CaCO_3$	Ca	13.0	480	980	80	55	110	55
Magnesite	$MgCO_3$	Mg	4.3	20	45	7.0	5.6	8.0	4.4

*Values above 20 µg/ml and 100 µg/ml rounded to nearest 5 and 10 respectively.

†Metal in solution calculated from 3 hour run.

of distilled H_2O under a CO_2 enriched atmosphere as a solvent of minerals. On the basis that humic acids are approximately 60% C it follows that 50 ml of a 500 $\mu g/l$ solution could theoretically generate 28 ml of CO_2.

Samples of galena, pyrolusite, calcite, dolomite and magnesite, of grain size range 0.30 to 0.60 mm, were exposed to distilled H_2O under an atmosphere of 22 ml air and 28 ml CO_2 for a period of 24 hours. These experiments were carried out with the experimental arrangement shown in Figure 11. With the mineral sample in place, the whole vessel is filled with distilled water. The CO_2, air and humic acids (as a concentrated solution) are introduced at the top and the displaced H_2O removed at the bottom. The averaged results for this experiment are given in Table 9 and the complete analytical data in Appendix 1, Table 14. These show that the presence of high concentrations of CO_2 increases the solubility of minerals and, as would be expected, the carbonates are most affected. The results obtained with the 500 $\mu g/l$ solution of THA-1 however, indicate that humic acids are far more aggressive than is the CO_2 that would result from their decay. This does not support the claim by Blanck (1933) that the weathering phenomena observed in the presence of humic acids are largely due to increased CO_2.

4.6 *The action of humic acids on silicates*

Although the writer's interest is largely in minerals of economic deposits, the solubility of a few silicates in humic acids was investigated. Samples of perthitic feldspar, biotite, enstatite, actinolite and epidote were prepared in the same manner as the non-silicates and were subjected to the action of the 1 g/l solution of THA-1 for a period of 5 days. The results are given in Table 10.
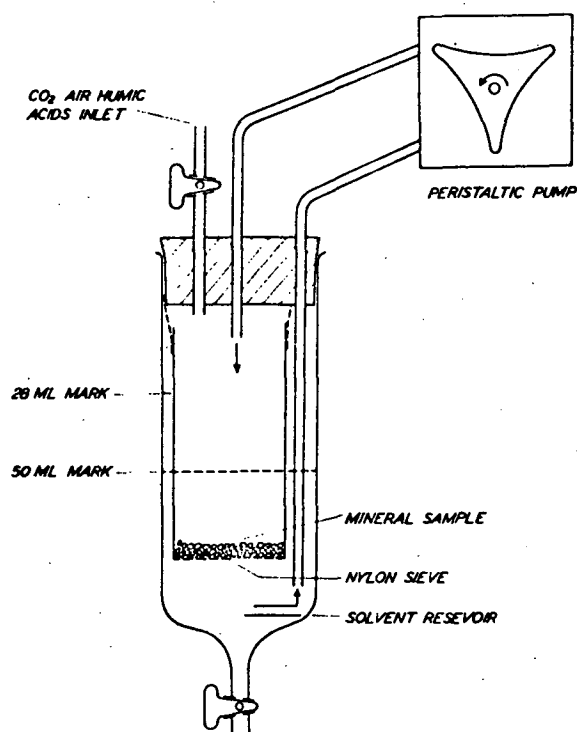
Figure 11. *Experimental arrangement for study of interaction between H₂O/CO₂ enriched air and minerals.*

Table 9. REACTION OF MINERALS WITH H₂O/ATMOS. CO₂, H₂O/CO₂ ENRICHED AIR AND A 500 mg/l THA-1 SOLUTION.

Mineral	Element determined	μg/ml metal* in solution after 24 hours extraction by:		
		H₂O/atmos. CO₂	H₂O/CO₂ enriched air	500 mg/l THA-1
Galena	Pb	1.1	4.7	50
Pyrolusite	Mn	3.3	4.2	30
Calcite	Ca	13.0	55	350
Dolomite	Ca	4.9	9.0	150
	Mg	2.7	6.6	110
Magnesite	Mg	4.3	5.5	20

*Values above 20 μg/ml and 100 μg/ml rounded to nearest 5 and 10 respectively.

Table 10. REACTION OF SILICATES WITH H_2O/ATMOS. CO_2 AND A 1 g/l
SOLUTION OF THA-1

| Mineral | Element determined | μg/ml* metal in solution after 5 days extraction by: | |
		H_2O/atmos. CO_2	1 g/l THA-1
Alkali	Na	3.4	12.6
feldspar	K	1.9	6.4
$(Na,K)AlSi_3O_8$	Al	<0.1	2.2
	Si	<0.1	<0.1
Biotite	K	0.6	1.0
$K(Mg,Fe)_3$	Mg	0.2	0.9
$(AlSi_3O_{10})(OH)_2$	Fe	<0.1	2.4
	Al	<0.1	3.0
	Si	<0.1	0.1
Enstatite	Mg	0.8	6.2
$(Mg,Fe)SiO_3$	Fe	<0.1	2.2
	Si	<0.1	<0.1
Actinolite	Mg	0.3	0.8
$Ca(Mg,Fe)$	Fe	<0.1	9.6
$(Si_8O_{22})(OH,F)_2$	Ca	7.5	30
	Si	<0.1	0.4
Epidote	Ca	18.0	110
$CaFeAl_2O.OH$	Fe	0.1	13.0
$(Si_2O_7)(SiO_4)$	Al	0.4	3.2
	Si	<0.1	0.1

*Values above 10 μg/ml and 100 μg/ml rounded to nearest
5 and 10 respectively

Whilst the silicate minerals are more resistant to attack than other

minerals studied, the amount of metal removed by the humic acids is

impressive. Biotite appears the least affected whilst epidote has

been vigorously attacked.

Because of differing experimental arrangements, it is not

possible to make a direct comparison with the studies of other

investigators. The high extraction of K, Mg, Ca and Fe relative to

Si and Al supports the claim of Schalsha et al. (1967) that the metals

are removed from the silicate framework by complexation. The results

obtained by Ponomareva and Ragim-Zade (1969) for pulverised samples

of feldspar and biotite showed that the removal of K, Na, Fe and Mg

by fulvic and humic acids exceeded that of Si and Al, although

considerable amounts of the latter two elements were found in the leach solutions. For the present series of experiments, with coarser grained samples, far higher relative extraction of metals other than Si and Al has been found.

4.7 The action of humic acids on metals

Since the experiments with minerals suggest that humic acids are strong solvents, experiments were carried out to determine the effect of 500 mg/l solutions of THA-1 and THA-4 on a number of metals. Analytical grade powders of iron, copper, lead, zinc, bismuth and antimony were sieved through 0.15 mm mesh cloth and the fines were washed out by repeated stirring in water. Weights of one-tenth the specific gravity of the respective metals were supported in fritted glass crucibles and exposed to the action of 50 ml volumes of the humic acids. The solutions were circulated through the metals for 15 minutes by means of a peristaltic pump.

The average results are given in Table 11 and the complete analytical data in Appendix 1 show that all metals except antimony are appreciably more soluble in the solutions of humic acids than in H_2O/atmos. CO_2. The maximum solubility is displayed by lead with an extraction of 260 µg/ml by THA-1, which had to be estimated from

Table 11. REACTION OF METALS WITH H_2O/ATMOS. CO_2 AND 500 mg/l SOLUTIONS OF THA-1 AND THA-4.

Metal	µg/ml* metal in solution after 15 minutes extraction by:		
	H_2O/atmos. CO_2	500 mg/l THA-1	500 mg/l THA-4
Iron	1.3	45	25
Copper	<0.1	35	25
Lead†	70	260	200
Zinc	0.3	70	50
Bismuth	<0.1	14.5	5.0
Antimony	30	30	25

*Values above 20 g/m and 100 g/m rounded to nearest 5 and 10 respectively.

†Metal extracted calculated from 5 minute run.

a 5 minute run because of the speed of the reaction. The solubility

of antimony in humic acids is not significantly different from that

in H_2O/atmos. CO_2. As was the case with the sulphides of these metals,

antimony behaves in a very different manner from bismuth.

4.8 Summary

The results of experimental studies reported in this chapter,

which attempt to simulate conditions in nature, leave no doubt about

the potential of humic acids in mineral degradation. It is possible

that the activity of humic acids is greatest where they are generated

in soils of podzolic affinities, and under cool temperate, high

rainfall climatic conditions.

The minerals commonly associated with ore deposits are, with

few exceptions, rapidly attacked by solutions of humic acids. The

result of these reactions must be the introduction of some

association of humic acids and cations into the weathering cycle.

It remains in the following chapters to investigate the characteristics

of this association.

CHAPTER 5

pH AND POTENTIOMETRIC TITRATION STUDIES OF THE INTERACTION BETWEEN
HUMIC ACIDS AND CATIONS

Martell and Calvin (1952) have commented that the reaction of

a complexing agent with a cation is accompanied by a decrease in pH.

The extent of displacement of H^+ from the complexing agent is a

measure of the strength of the complex formed. This is true only if

the reaction under study is solely one of complexation. In the case

of humic acids, the occurrence of ion exchange and possibly, in view

of the complexity of these substances, more obscure phenomena are

likely to complicate the results of pH studies.

When titrations of solutions of metal ions with a base are

monitored by pH measurements, the formation of metal hydroxides is

indicated by inflections in the titration curves. In the presence

of an excess of a complexing agent, no hydroxides are formed and

hence there are no inflections in the titration curves. Use was made

of these two pH dependent techniques to obtain information on the

interaction of the Tasmanian samples of humic acids with a number of

cations.

5.1 *pH variation on interaction of humic acids with cations*

The general pH effect accompanying the interaction between

humic acids and various cations was investigated in the following

manner. Bulk solutions of THA-1 and THA-4 containing 1 g/*l* humic

acids were prepared, and adjusted to pH = 4 with NaOH. To 50 ml

aliquots of these were added 2 ml of 100 µ eq/m*l* solutions of Ag^{+1},

Ca^{+2}, Co^{+2}, Cu^{+2}, Mg^{+2}, Ni^{+2}, Pb^{+2} and Zn^{+2}. This procedure was

carried out in duplicate and the decreases in the pH values

accompanying the interactions were measured. Although use was made

of a Townson 0.001 pH resolution digital instrument and a Schott Mainz

N61 electrode, it would seem that in electrochemical studies,

humic acids display their greatest perversity. The pH of the systems fluctuated widely with time and although the results are given in 0.01 pH units in Table 12 it is unlikely that the values are better than ±0.05.

The results suggest that Pb^{+2} and Cu^{+2} are most strongly bound to the humic acids whilst Mg^{+2} is the most weakly bound of the divalent metals. Silver, although univalent, is held to the same degree as Mg^{+}. For Ca^{+2}, Co^{+2}, Mn^{+2}, Ni^{+2} and Zn^{+2} the pH effects lie between those for Cu^{+2} and Mg^{+2} and, whilst the order varies, the differences for each humic acid sample are small. The data for all metals indicate that the strength of cation binding decreases in the order THA-1 > THA-3 > THA-2 > THA-4 > THA-5.

5.2 Hydrogen ion and cation balances on interaction of humic acids and cations

Experiments were carried out with THA-1 and THA-4 to monitor the hydrogen ion release and cation retention by these samples of humic acids. In these experiments use was made of dialysis tubes to separate free from bound cations. The dialysis bags, containing 5 ml of 1% (w/v) THA-1 or THA-4 and 5 ml of distilled water were lowered into test tubes containing 40 ml of distilled water. The systems were allowed 48 hours to reach equilibrium and the pH values were measured. Next, 2 ml of water was removed from each of the test tubes and 2 ml of 100 µ eq/ml cation solutions added inside the dialysis bags. After a further 48 hours the pH values and metal contents of the solutions in the test tubes were determined. The reservations expressed about pH measurements in humic acid solutions also apply to these experiments.

The initial pH values of the THA-1 and THA-4 solutions in distilled H_2O averaged 3.30 and 3.31 respectively. This means that

Table 12. *DECREASE IN pH ACCOMPANYING HUMIC ACID INTERACTION WITH CATIONS*

THA-1		THA-2		THA-3		THA-4		THA-5	
Cation	ΔpH	Cation	ΔpH	Cation	ΔpH	Cation	ΔpH	Cation	ΔpH
Pb^{+2}	1.04	Pb^{+2}	0.93	Pb^{+2}	1.02	Pb^{+2}	0.74	Pb^{+2}	0.58
Cu^{+2}	0.95	Cu^{+2}	0.71	Cu^{+2}	0.84	Cu^{+2}	0.64	Cu^{+2}	0.53
Ni^{+2}	0.74	Ni^{+2}	0.53	Zn^{+2}	0.66	Ni^{+2}	0.41	Ni^{+2}	0.35
Co^{+2}	0.71	Mn^{+2}	0.52	Ni^{+2}	0.65	Co^{+2}	0.40	Co^{+2}	0.33
Ca^{+2}	0.68	Co^{+2}	0.51	Co^{+2}	0.61	Mn^{+2}	0.35	Mn^{+2}	0.31
Mn^{+2}	0.67	Zn^{+2}	0.50	Mn^{+2}	0.60	Ca^{+2}	0.34	Ca^{+2}	0.30
Zn^{+2}	0.64	Ca^{+2}	0.48	Ca^{+2}	0.58	Zn^{+2}	0.34	Zn^{+2}	0.27
Mg^{+2}	0.51	Mg^{+2}	0.46	Mg^{+2}	0.46	Mg^{+2}	0.23	Ag^{+1}	0.23
Ag^{+1}	0.46	Ag^{+1}	0.43	Ag^{+2}	0.40	Ag^{+1}	0.21	Mg^{+2}	0.18

the ionisation of the humic acids released approximately 25 μeq H^+.
Alternatively the THA-1 and THA-4 polyanions had available the
corresponding negative sites for cation combination. The final pH
and metal content determinations yielded values for the further
displacement of H^+ on the addition of cations and also the quantity
of metal bound to the humic acids. The average data are given in
Tables 13 and 14.

*Table 13. INTERACTION OF THA-1 AND CATIONS: pH, H^+ DISPLACEMENT
AND CATION BINDING*

Cation	pH after addition of cation	Total μeq H^+ released*	H^+ in excess of ionisation release	μeq cation bound*
Pb^{+2}	2.85	70	45	86
Cu^{+2}	2.93	58	33	70
Zn^{+2}	3.12	38	13	30
Ni^{+2}	3.12	38	13	36
Ca^{+2}	3.13	38	13	38
Mn^{+2}	3.14	36	11	38
Co^{+2}	3.16	34	9	38
Mg^{+2}	3.22	30	5	18
Ag^{+1}	3.24	28	3	20

*H^+ and μeq cations to nearest 2 μeq

When the pH values and the amount of metal bound by the humic
acids are compared, no clear relationship between cation binding and
H^+ displacement emerges. In the case of THA-1, which is generally
more effective than THA-4 in the binding of cations, the behaviour
of Pb^{+2} and Cu^{+2} differs from that of the other cations. For these
two, the quantities bound are greater than the amount of H^+ released
and hence a proportion of them must be held by some mechanism which
does not involve bonding to an anionic site. With Ag^{+1}, Ca^{+2}, Co^{+2},

Table 14. INTERACTION OF THA-4 AND CATIONS: pH, H^+ DISPLACEMENT AND CATION BINDING

Cation	pH after addition of cation	Total μeq H^+ released*	H^+ in excess of ionisation release	μeq cation bound*
Pb^{+2}	2.78	84	59	70
Cu^{+2}	2.81	78	53	62
Zn^{+2}	2.99	52	27	20
Ni^{+2}	2.99	52	27	24
Mn^{+2}	3.01	48	23	26
Co^{+2}	3.01	48	23	22
Ca^{+2}	3.02	46	21	14
Mg^{+2}	3.05	44	19	10
Ag^{+1}	3.07	42	17	14

*H^+ and μeq cations to nearest 2 μeq

Mn^{+2}, Ni^{+2} and Zn^{+2} the amount of cation binding approximates to the H^+ displaced. For Mg^{+2}, the initial ionisation would have provided sufficient sites. That there has been further displacement of H^+ on the addition of this cation indicates that a number of the ionisation sites are unacceptable and that some form of selectivity is operating.

The situation with THA-4 differs from THA-1, in that for all cations, the amount bound is less than the H^+ released as a result of interaction. There is a marked surplus of H^+ and only the amounts of Pb^{+2} and Cu^{+2} approximately balance the release of the former ion. For other cations it appears that none of the sites created by ionisation are utilised in cation binding. The reason for the differing behaviour of THA-1 and THA-4 probably lies in the structural arrangement of their functional groups, but with existing knowledge this must remain a matter for conjecture.

5.3 *Potentiometric titration of metals in the presence of humic acids*

Numerous potentiometric titration studies have been made of the possible complexation of metals by humic substances. Martin and Reeve (1958) found no evidence for the complexation of metals by fulvic acids. Beckwith (1959) however, concluded that humic acids complexed metals and that the stabilities of the metal humates were in accordance with the Irving-Williams series. Studies by Khanna and Stevenson (1962), Khan (1969) and Van Dijk (1971) have all indicated the formation of metal complexes with humic acids, although Van Dijk has found that the stability of the complexes do not follow the Irving-Williams series.

In this study, 500 µeq of Ag^{+1}, Co^{+2}, Cu^{+2}, Ni^{+2}, Pb^{+2} and Zn^{+2} in 50 ml of 0.1 KCl (KNO_3 in the case of Ag^{+1}) were titrated with 0.1 meq/ml NaOH. These titrations were repeated in the presence of an excess of THA-1 and THA-4 (0.2 g). In order to assess the effects of adsorption phenomena on the titrations, these were also carried out in the presence of 0.2 g MnO_2. The potentiometric titrations were carried out manually and the pH values measured with the same equipment as in the preceding studies. The titration curves that were drawn from the results are shown in Figures 12 and 13. The measurements from which these diagrams were produced are given in Appendix 3.

The titration curves for the cations studied exhibit inflections in the regions of hydroxide precipitation. In Figure 12, these are seen for Co^{+2}, Cu^{+2} and Pb^{+2} at pH values of about 8.5, 5.0 and 5.8 respectively. For Ni^{+2}, Ag^{+1} and Zn^{+2} (fig. 13) the respective pH values are about 8.5, 9.2 and 7.8. Adsorption of the cations on MnO_2 prior to potentiometric titration modifies their behaviour to varying degrees. The presence of MnO_2 has only minor effect on the
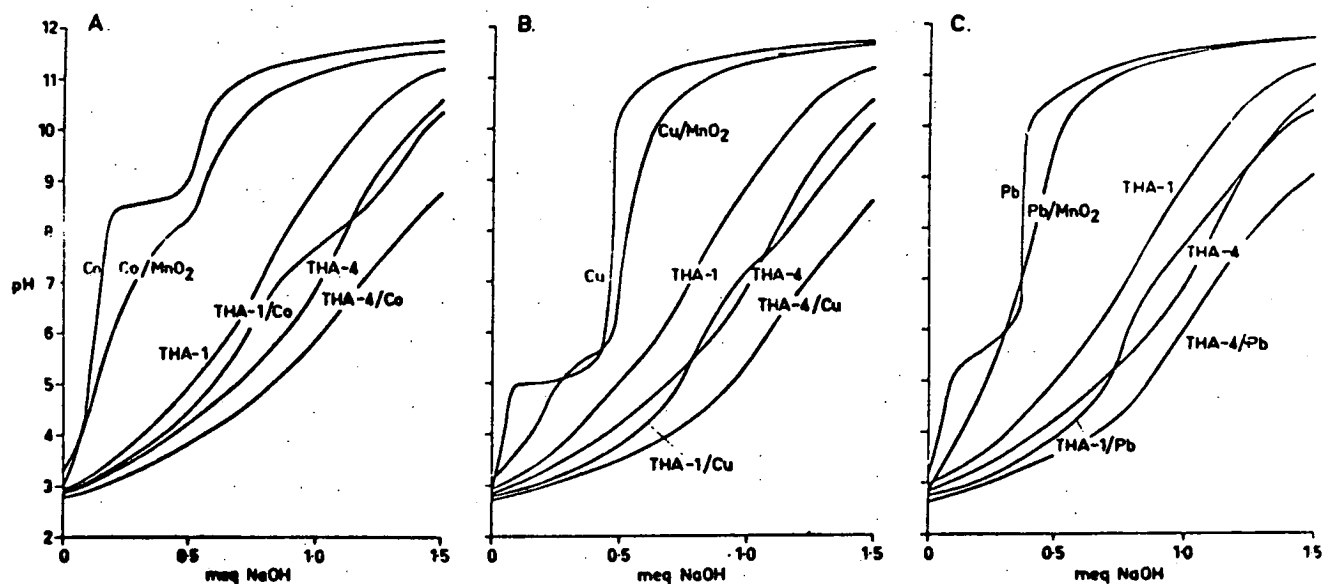
Figure 12. *Potentiometric titration curves for 500 μ eq of (A) cobalt, (B) copper and (C) lead, alone and in the presence of 0.2 g MnO$_2$, THA-1 and THA-4.*

titration of Ni^{+2} (fig. 13A) and Zn^{+2} (fig. 13C) in that a moderately strong inflection, which indicates the formation of hydroxides, is still present for these cations. For Co^{+2} (fig. 12A) and Cu^{+2} (fig. 12B) the inflections are less marked in the presence of MnO$_2$, whereas for Pb^{+2} (fig. 12C) and Ag^{+1} (fig. 13B) they are absent. Whilst the adsorption on MnO$_2$ modifies the titration curves to some extent, they all follow the same general path as for the cations alone.

In the case of the humic acids THA-1 and THA-4, the titration curves are of the typical sigmoidal form. This indicates that THA-1 and THA-4 titrate in a manner similar to monobasic acids. With the titrations of the humic acids in the presence of the various cations there is no development of inflections due to hydroxide formation.
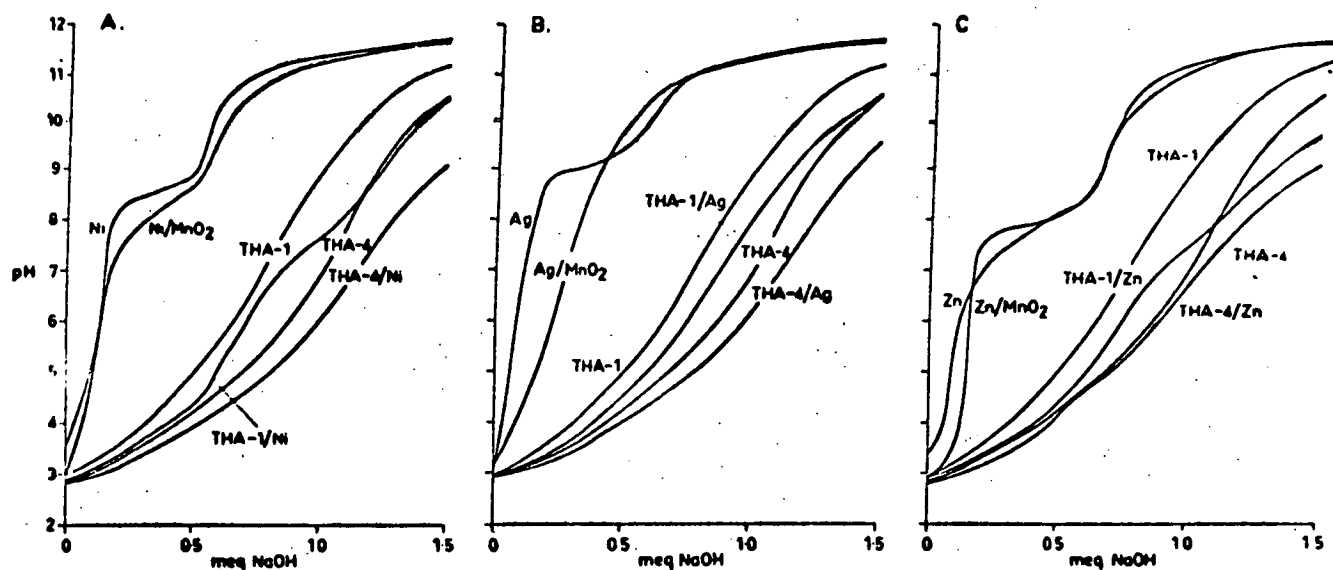
Figure 13.   *Potentiometric titration curves for 500 µ eq of (A) nickel, (B) silver and (C) zinc, alone and in the presence of 0.2 g MnO_2, THA-1 and THA-4.*

For all cations studied these titration curves are displaced from the path followed by humic acids alone, as would be expected in the event of complex formation (Martell and Calvin, 1952). It is thus apparent that, although the pH effects attending interaction of humic acids with cations have many obscure features, they confirm that such interaction is at least in part complexation.

CHAPTER 6

POLAROGRAPHIC STUDIES OF THE INTERACTION BETWEEN HUMIC ACIDS AND CATIONS

Lingane (1941) demonstrated that polarographic analysis could be applied to the study of metal complexation. Changes in the state of metal from ionic to complexed, or from one complex to another are generally evident in the characteristics of the relevant polarograms. Such changes are accompanied by variation in the position of the half-wave potential $(E_{\frac{1}{2}})$ for a particular reduction and in the value of the diffusion current (I_d) associated with this event. The effect of humic acids on the polarographic reduction of metals thus yields information on their complexation. Since reduction processes are involved, polarographic studies may also be used to examine the reduction characteristics of humic acids. The high electrolyte concentration necessary to carry the current in polarographic analysis causes problems with the solubility of humic acids. The method can be applied however, by making use of supporting electrolytes that are alkaline, organic salts of alkali metals or combinations of these.

6.1 *Complexation of metals by humic acids*

Studies of complexation by humic acids were undertaken by carrying out polarographic reduction of 1 μ mole/ml solutions of Pb^{+2}, Cd^{+2} and Cu^{+2} in the absence and presence of 0.1% THA-1 and THA-4. The supporting electrolyte in the case of Pb^{+2} and Cu^{+2} was an alkaline solution of sodium citrate (0.1 M NaOH-1M $Na_3C_6H_5O_7$). For the Cd^{+2} study the supporting electrolyte was alkaline NH_4Cl (1M NH_4OH-1M NH_4Cl). Polarograms were recorded by means of DC pulsed polarography using a Bruker E 1000 unit. These are illustrated in Figures 14, 15 and 16.

In the case of Pb^{+2} (fig. 14A) the $E_{\frac{1}{2}}$ value in the citrate electrolyte without humic acids was found to be -0.66 V* with an I_d value of 3.7 μA. In the presence of both THA-1 and THA-4 (fig. 14B) the $E_{\frac{1}{2}}$ and I_d values were respectively -0.65 V and 3.0 μA.

*All potentials are relative to the saturated calomel electrode.
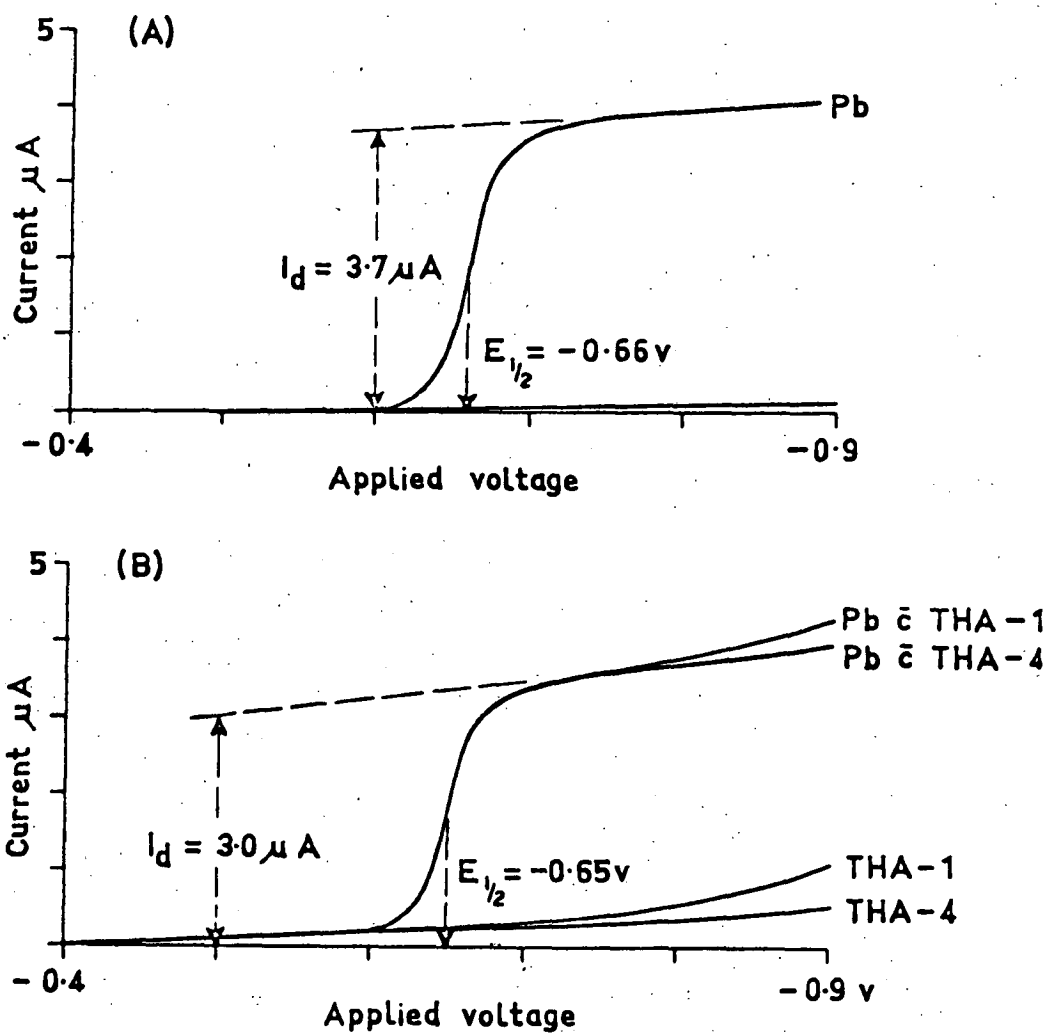
Figure 14. *Polarograms of 1 μ mole/ml Pb^{+2} in 1M Na$_3$C$_6$H$_5$O$_7$-0.1 M NaOH. (A) Pb^{+2}. (B) Pb^{+2} c̄ 50 mg THA-1 and THA-4.*
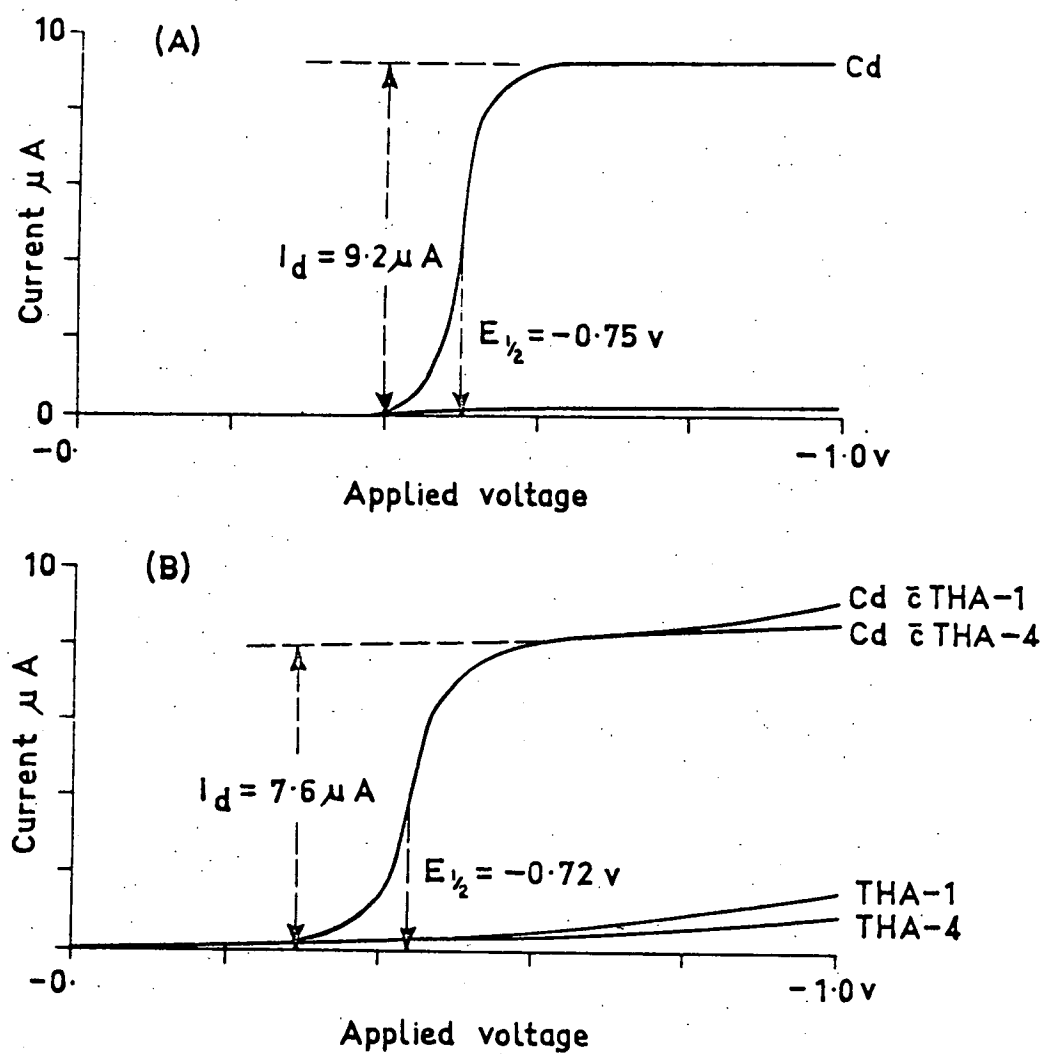
Figure 15. *Polarograms of 1 μ mole/ml Cd^{+2} in 1 M NH₄OH/1 M NH₄Cl. (A) Cd^{+2}. (B) Cd^{+2} c̄ 50 mg THA-1 and THA-4.*
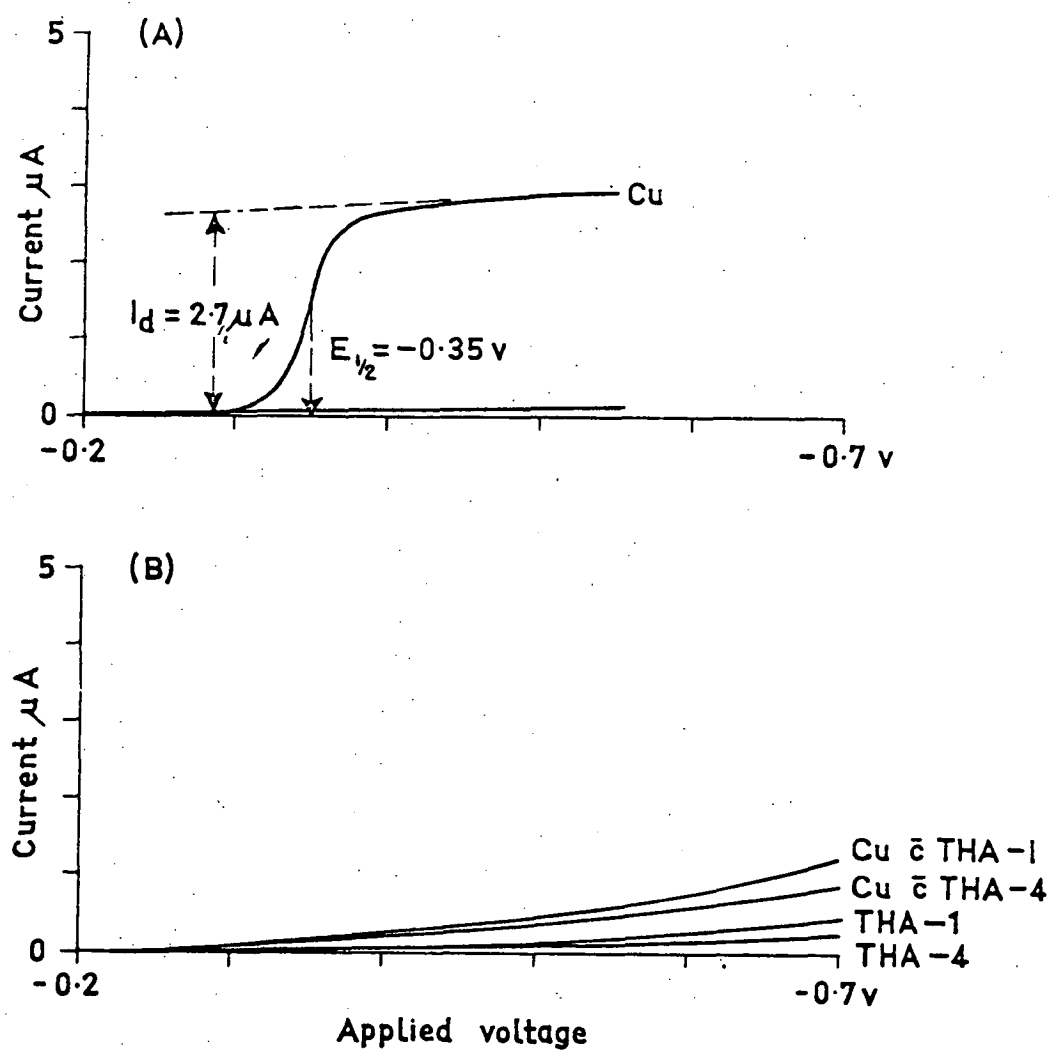
Figure 16. *Polarograms of 1 μ mole/ml Cu+2 in 1 M Na₃C₆H₅O₇/
0.1 M NaOH. (A) Cu+2. (B) Cu+2 c̄ 50 mg THA-1 and THA-4.*

These minor changes in the characteristics of the polarographic waves for the reduction of Pb^{+2} suggests that the stability constants of the complexes formed in the presence of THA-1, THA-4 and alkaline citrate are of the same order of magnitude.

The polarograms for Cd^{+2} (fig. 15A) showed that the $E_{\frac{1}{2}}$ value in the absence of humic acids was -0.75 V and the I_d value was 9.2 μA. In the presence of both THA-1 and THA-4 (fig. 15B) the $E_{\frac{1}{2}}$ value was -0.72 V and I_d was 7.6 μA. Since the reduction occurs at a slightly less negative value in the presence of humic acids it appears that the complexes of Cd^{+2} with humic acids are of lower stability than that formed in the presence of alkaline NH_4Cl.

With Cu^{+2} (fig. 16A), polarographic reduction in alkaline citrate occurred at an $E_{\frac{1}{2}}$ value of -0.35 V with an I_d value of 2.9 μA. In the presence of THA-1 and THA-4 (fig. 16B) no polarographic wave was developed. It thus appears that the complexes formed with humic acids are sufficiently strong to prevent polarographic reduction of Cu^{+2}.

6.2 Reducing character of humic acids

A number of comments have been made in the literature concerning the reducing properties of humic acids. Dragunov et al. (1950) found reducing substances, such as carbohydrates, to be present in extracts of humic acids. Kononova (1966) stated that there could be no certainty that such substances were in fact a part of the humic acid molecule. Garrels and Pommer (1959) have suggested that lignin could reduce the uranyl ion to pitchblende and on this basis Ong and Swanson (1969) have given a value for the reduction potential of humic acids at least as low as +0.447 V. From a study of variation of E_h value with concentration of peat humic acids and pH, Szilagyi (1971) derived by extrapolation to pH = 0 a value for E_o of +0.7 V.

If reductions of metal ions, which can be studied by polaro-graphic procedures, occur at potentials close to the value assigned to humic acids then it should be possible to estimate the standard electrode potential of these substances from their effect on the polarographic reduction of the selected ions. The value of +0.7 V suggested by Szilagyi (1971) is supported by comprehensive laboratory studies and it was thus chosen as a basis for polarographic investigations. This value is slightly less than that for the standard reduction potential of ferric to ferrous iron: $Fe^{+3} + e \rightleftharpoons Fe^{+2}$ (0.770 V) and slightly greater than that for the reduction of hexavalent to quadrivalent uranium: $UO_2^{+2} + 4H^+ + 2e \rightleftharpoons U^{+4} + 2H_2O$ (+0.62 V). Polarographic studies were thus made of the reduction of Fe^{+3} and U^{+6} in the absence and presence of 0.1% THA-1 and THA-4.

The polarographic reduction of iron, $Fe^{+3} \rightarrow Fe^{+2} \rightarrow Fe^0$ can be studied in the presence of a tartrate supporting electrolyte. Polarograms of the reduction of 1 μ mole/ml solutions of iron, in ammonium tartrate adjusted to pH = 7 with tartaric acid (0.5 M $(NH_4)_2C_4H_4O_6-C_4H_4O_6$), were recorded in the absence and presence of 0.1% THA-1 and THA-4. The reduction $Fe^{+2} \rightarrow Fe^0$ usually occurs at a potential more negative than the discharge of H^{+2} (-1.6 V) and is thus obscured by this. In the tartrate electrolyte at pH = 7, however, slow attainment of equilibria for the various tartrate complexes present causes the reduction to produce two waves, one of which occurs at a potential less negative than the H^{+1} discharge. The polarograms for the reduction of iron are illustrated in Figure 17.

In Figure 17A the reduction of $Fe^{+3} \rightarrow Fe^{+2}$ is seen to occur with $E_{\frac{1}{2}}$ and I_d values of -0.30 V and 2.8 μA respectively. This is followed by the first wave for the reduction $Fe^{+2} \rightarrow Fe^0$ at $E_{\frac{1}{2}}$ and I_d values of -0.88 V and 1.1 μA respectively. In the presence of

THA-1 (fig. 17B) there is no sign of the reduction of $Fe^{+3} \rightarrow Fe^{+2}$

but the first wave of the reduction $Fe^{+2} \rightarrow Fe^0$ occurs with $E_{\frac{1}{2}}$ and

I_d values of -0.94 V and 1.8 μA respectively. With THA-4 (fig. 17C)

similar result is apparent and the values of $E_{\frac{1}{2}}$ and I_d are -1.05 V

and 1.9 μA respectively. These results indicate that humic acids

reduce Fe^{+3} to Fe^{+2}, thus removing the relevant wave from the

polarogram. The displacement of $E_{\frac{1}{2}}$ values for the reduction

$Fe^{+2} \rightarrow Fe^0$ of -0.88 V to -0.94 V and -1.05 V in the presence of THA-1

and THA-4 respectively, indicates that the complexes of Fe^{+2} with

humic acids are more stable than the tartrate complex. Since humic

acids are capable of reducing Fe^{+3} it appears that the standard

reduction potential of these substances is lower than that for the

reduction $Fe^{+3} + e \rightleftharpoons Fe^{+2}$ of +0.770 V.

For the study of the polarographic reduction of $U^{+6} \rightarrow U^{+4}$ a

supporting electrolyte of alkaline sodium citrate was used

(1 M $Na_3C_6H_5O_7$-0.1 M NaOH). Polarograms for the reduction of uranium

in the absence and presence of THA-1 and THA-4 are illustrated in

Figure 18. In the absence of humic acid (fig. 18A) polarographic

reduction occurred with $E_{\frac{1}{2}}$ and I_d values of -0.93 V and 2.0 μA

respectively. In the presence of THA-1 (fig. 18B) reduction occurred

with values for $E_{\frac{1}{2}}$ and I_d of -1.11 V and 0.7 μA respectively. In

the case of THA-4 (fig. 18C) the relevant values of $E_{\frac{1}{2}}$ and I_d were

1.25 V and 0.5 μA. This indicates that the standard reduction

potential of humic acid is higher than that for the reduction UO_2^{+2}

+ $4H^+$ 2e $\rightleftharpoons U^{+4}$ + $2H_2O$ of +0.62 V. It is also apparent that the

complexes of THA-1 and THA-4 with the uranyl ion are stronger than

that with citrate.
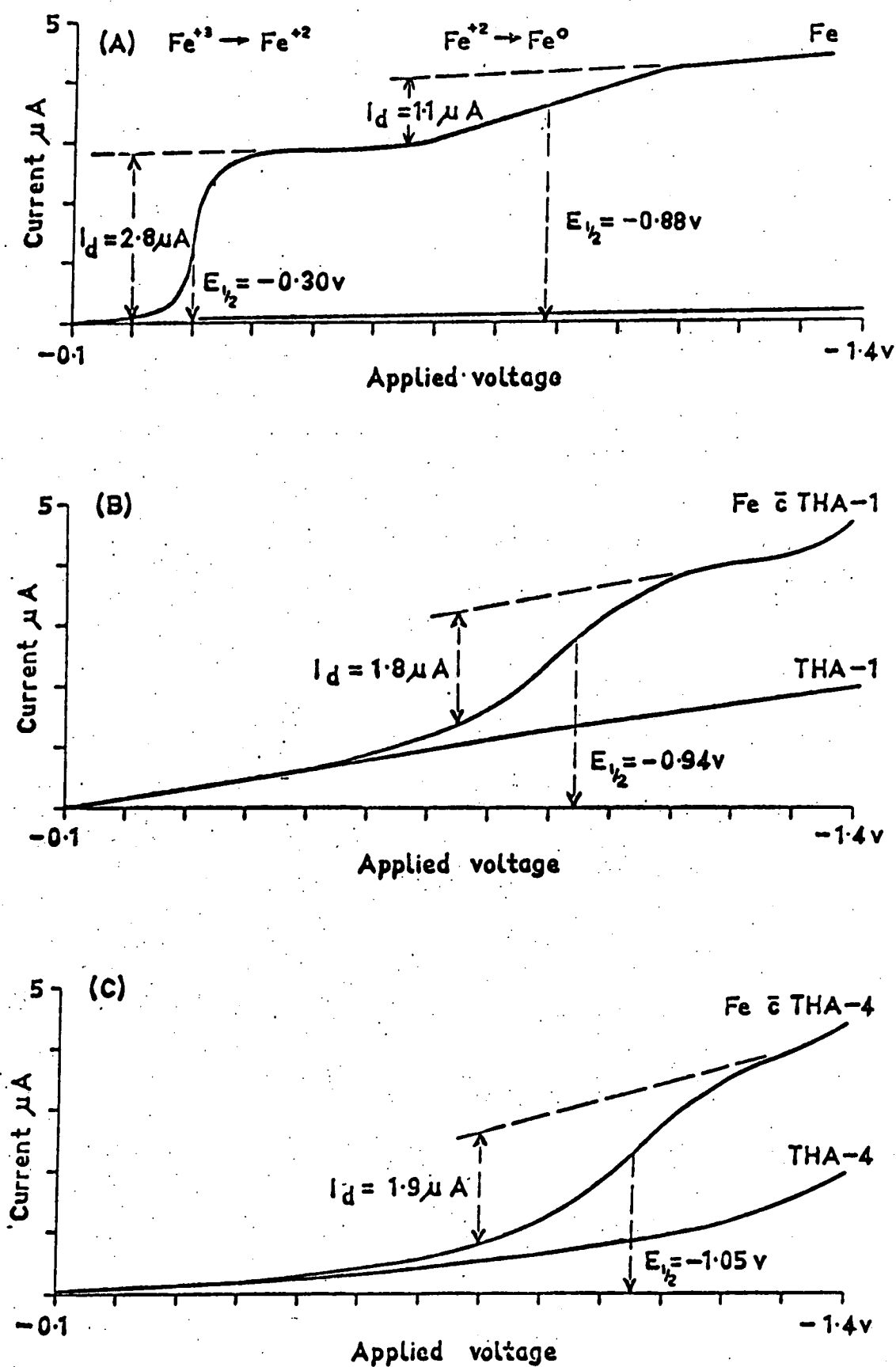
Figure 17. *Polarograms of 1 µ mole/ml Fe^{+3} in 0.5 N $(NH_4)_2C_4H_4O_6/pH = 7$ (A) Fe^{+3}. (B) Fe^{+3} c̄ 50 mg THA-1. (C) Fe^{+3} c̄ 50 mg THA-4*
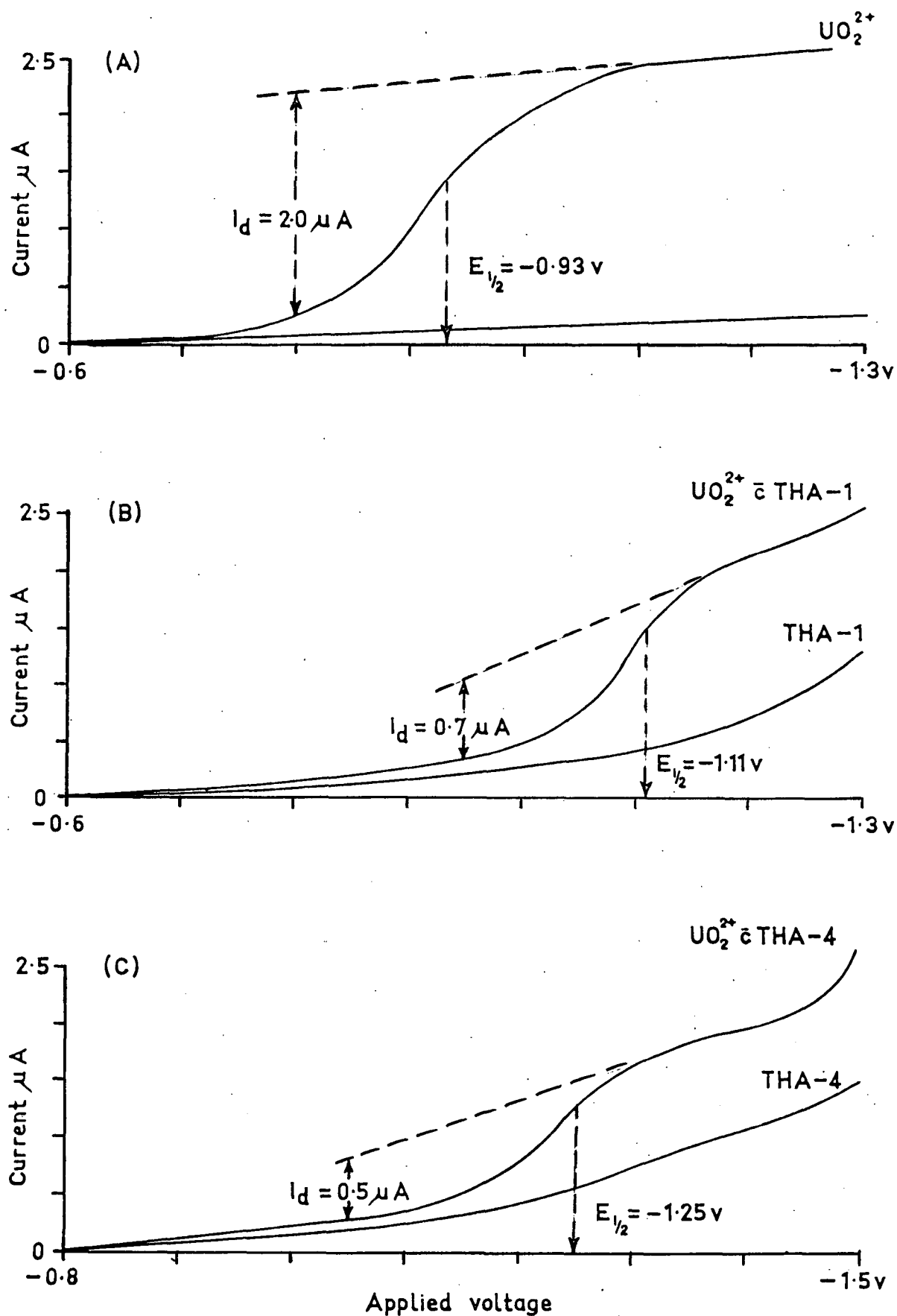
Figure 18. *Polarogram of 1 μ mole/ml UO₂⁺2 in 1 M Na₃C₆H₅O₇/*
0.1 M NaOH. (A) UO₂⁺2. (B) UO₂⁺2 c̄ THA-1
(C) UO₂⁺2 c̄ THA-4.

6.3 *Summary*

The polarographic studies described above confirm that one of

the possible interactions between humic acids and metals involves

complexation. The strength of complexes formed is widely variable.

In the investigations of Pb^{+2}, Cu^{+2} and UO_2^{+2}, which were undertaken

in a supporting electrolyte of alkaline citrate, the strength of

the complexes between Pb^{+2} and humic acids were of the same order

of magnitude as the citrate complex. The complexes of UO_2^{+2} with

humic acids were considerably stronger than that with citrate whilst

the complexes with Cu^{+2} were so strong that they prevented polarographic

reduction. The results of the comparative studies of Fe^{+3} and U^{+6}

are compatible with a standard reduction potential of humic acids of

+0.7 V, which was calculated by Szilagyi (1971).

CHAPTER 7

MISCELLANEOUS INVESTIGATIONS OF THE INTERACTION BETWEEN
HUMIC ACIDS AND VARIOUS INORGANIC SUBSTANCES

A number of procedures are available which may be used to
provide information about the characteristics of reactions of humic
acids with inorganic substances. In this chapter the attempts to
make use of X-ray diffraction, electrophoresis, infra-red spectroscopy,
leaching capabilities of humic acids, reaction kinetic studies and
comparative stability studies will be discussed.

7.1 *X-ray diffraction*

The fate of crystalline materials when they react with humic
acids should be indicated in X-ray diffractograms of the reactants
and the products of any reaction. In a series of experiments with
metal hydroxides and humic acids Ong *et al.* (1970) suggested that
soluble metal was maintained by the peptising of the hydroxides. If
this is the case, then the patterns for the hydroxides should be
observed in X-ray diffractograms of the dried mixture of hydroxides
and humic acids. In order to investigate the interaction of humic
acids and hydroxides, 5 mg each of $Zn(OH)_2$ and $Ni(OH)_2$ were mixed
with 5 ml of a 1% solution of THA-1 and agitated for a period of
three days. The solutions were then dried and X-ray diffraction
patterns obtained from the resulting powders. Patterns were also
obtained from physical mixtures of 5 mg each of $Zn(OH)_2$ and $Ni(OH)_2$
with 50 mg of THA-1.

These patterns are shown in Figure 19. In the case of $Zn(OH)_2$,
the sharp peaks recorded for the (110) and (101) planes at 2θ values
of 20.1° and 20.8° respectively (fig. 19A) from the physical mixture
of the hydroxide and humic acids are absent from the sample obtained

from the solution of THA-1 (fig. 19B). This leaves no doubt that the interaction between humic acids and $Zn(OH)_2$ has resulted in destruction of the hydroxide to form amorphous zinc humates rather than a peptising of the $Zn(OH)_2$. A similar situation was also found for the $Ni(OH)_2$, with a sharp diffraction from (101) planes at a 2θ value of 38.5° occurring in the pattern for the physical mixture (fig. 19C), whereas for the product of the solution experiment the diffraction from these planes is almost absent (fig. 19D). The weak response which was recorded for the (101) planes indicates that the reaction had not been completed during the three day period.

The same type of study was made for metallic lead and the lead minerals galena, anglesite and cerussite. The resulting comparative X-ray diffractograms are shown in Figures 20 and 21. For metallic lead the peak produced by diffraction from the (111) planes at a 2θ value of 31.3° (fig. 20A) is absent from the sample which was agitated for three days with the solution of THA-1 (fig. 20B). A similar result is seen in the diffraction from the (111) and (021) planes of cerussite at 2θ values of 24.8° and 25.5° respectively (fig. 20C, 20D). It is thus apparent that both metallic lead and cerussite have dissolved to form amorphous lead humates. For anglesite, the comparative diffraction from the (210) and (102) planes at 2θ values of 26.7° and 27.7° respectively (fig. 21A, 21B), indicate that this mineral has not been completely destroyed during the three day exposure to the solution of THA-1. In the case of galena, the diffraction results from the (111) planes at a 2θ value of 26.0° (fig. 21C, 21D), indicate that this mineral is the least affected of the lead minerals. These results are in keeping with the relative values for lead taken into solution by 1 g/1 THA-1 in 24 hours, of 291 000, 218 000, 96 000 and 3000, μg/ml from metallic lead, cerussite, anglesite and galena respectively (Baker, 1973).
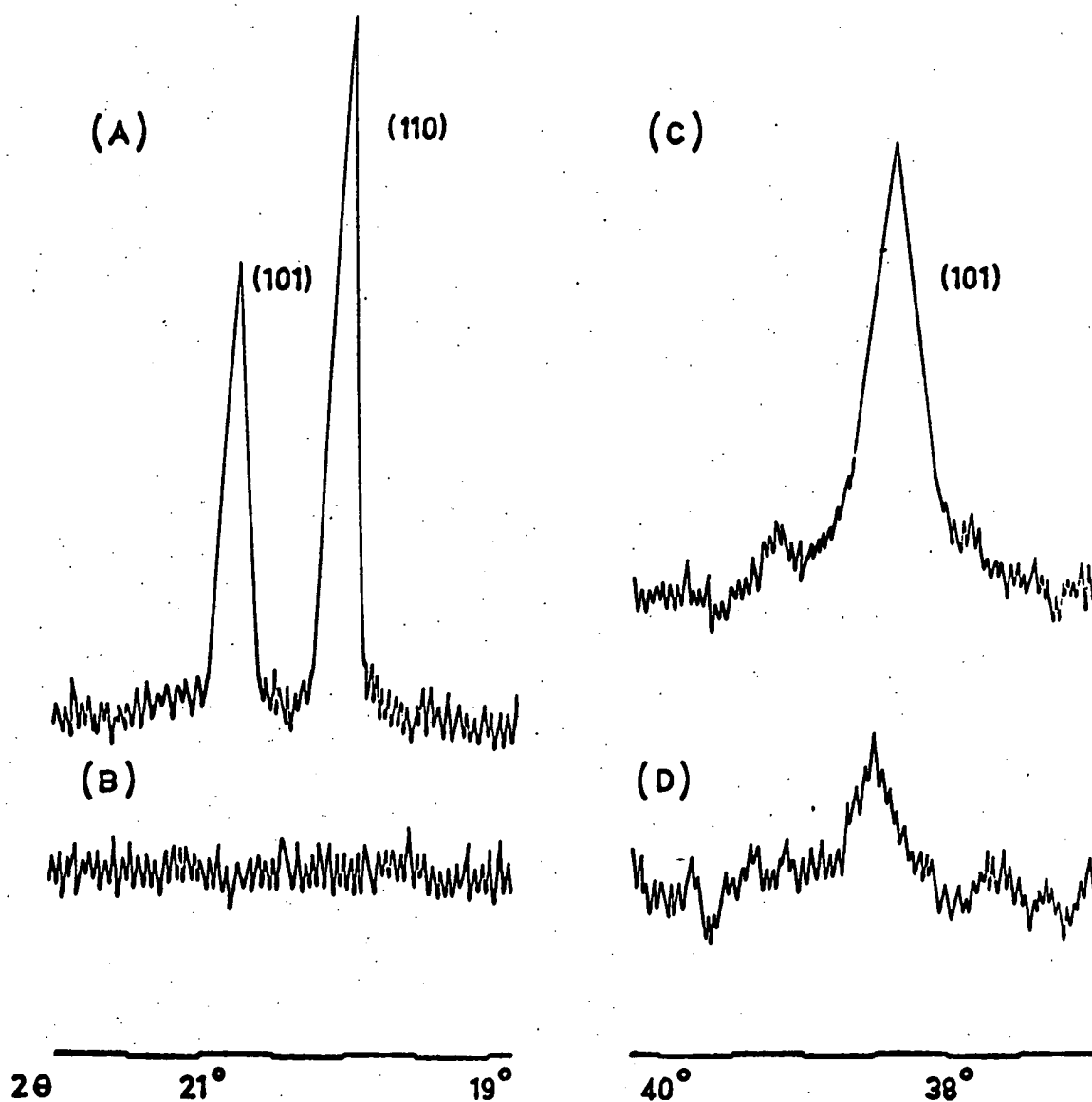
Figure 19. *X-ray diffraction patterns from:*

(A) *Physical mixture of 5 mg Zn(OH)$_2$ with 50 mg THA-1.*

(B) *Reaction product of 5 mg Zn(OH)$_2$ in 5 ml 1% solution of THA-1 after 3 days.*

(C) *Physical mixture of 5 mg Ni(OH)$_2$ with 50 mg THA-1.*

(D) *Reaction product of 5 mg Ni(OH)$_2$ in 5 ml 1% solution of THA-1 after 3 days.*
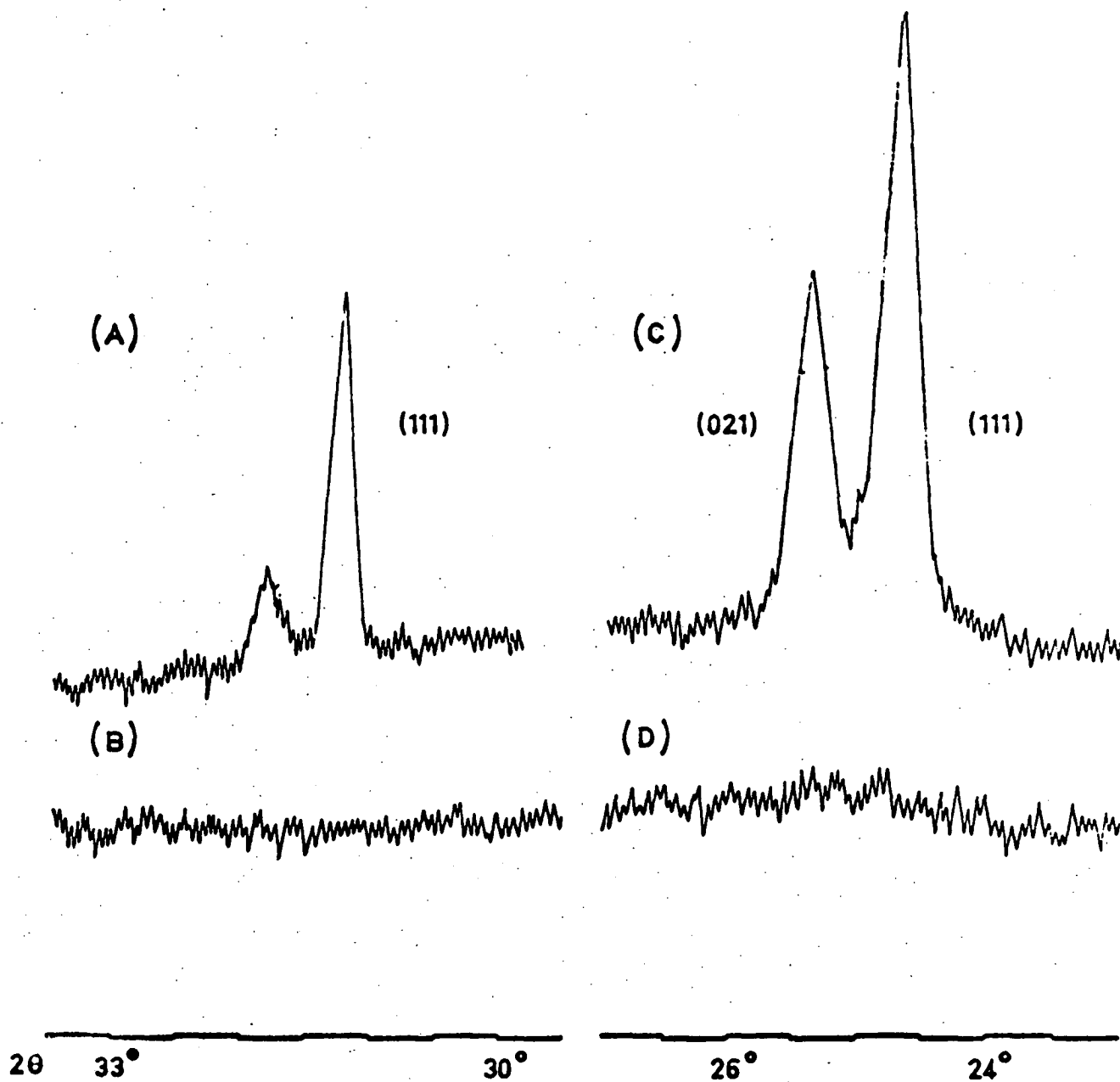
Figure 20. X-ray diffraction patterns from:

(A) Physical mixture of 5 mg metallic lead with 50 mg THA-1.

(B) Reaction product of 5 mg metallic lead in 5 ml 1% solution of THA-1 after 3 days.

(C) Physical mixture of 5 mg cerussite with 50 mg THA-1.

(D) Reaction product of 5 mg cerussite in 5 ml 1% solution of THA-1 after 3 days.
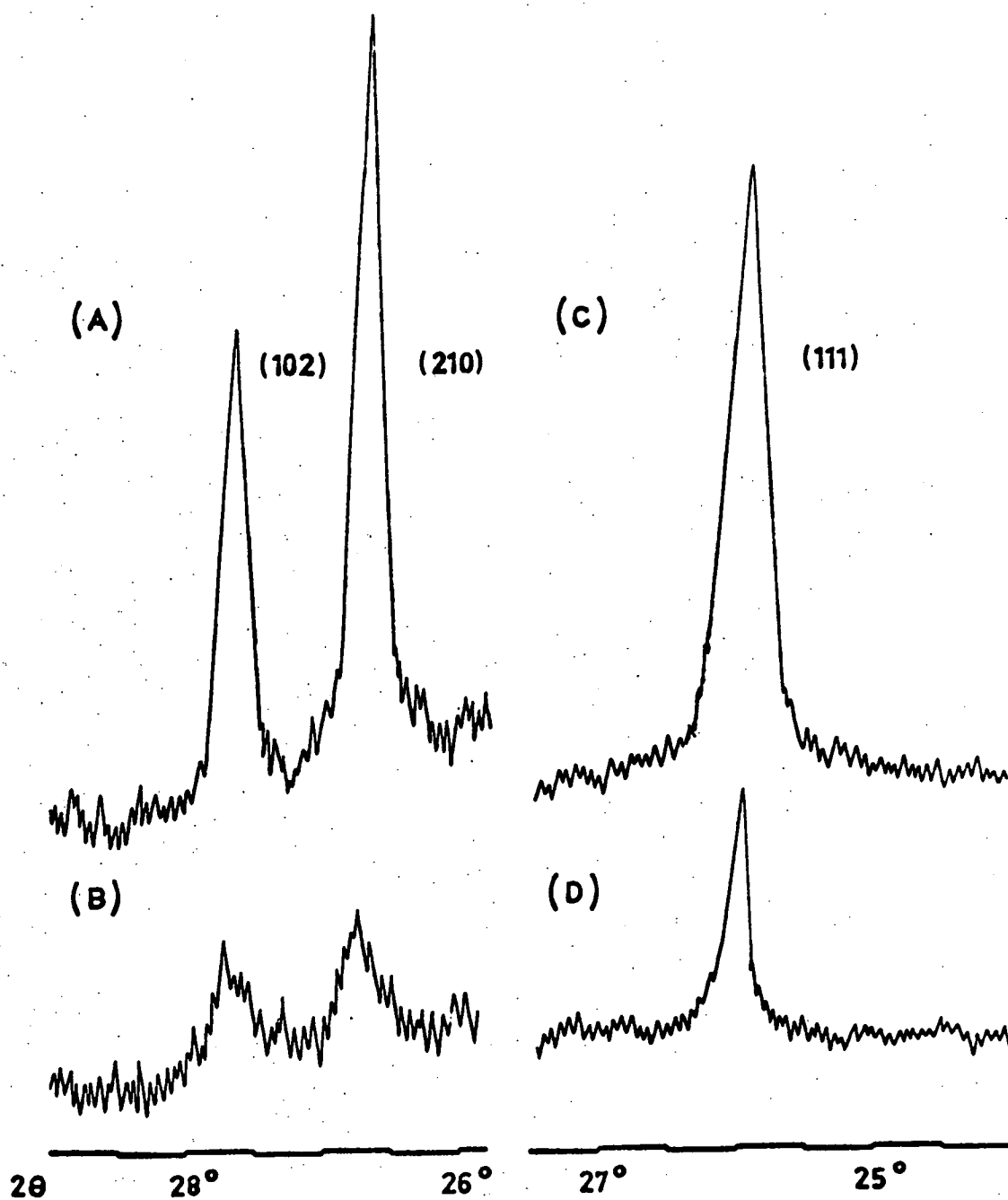
Figure 21. *X-ray diffraction patterns from:*

   (A)   Physical mixture of 5 mg anglesite with 50 mg THA-1.

   (B)   Reaction product of 5 mg anglesite in 5 ml 1% solution of THA-1 after 3 days.

   (C)   Physical mixture of 5 mg galena with 50 mg THA-1.

   (D)   Reaction product of 5 mg galena in 5 ml 1% solution of THA-1 after 3 days.

7.2 Electrophoresis of humic acids in the presence of cations

Electrophoresis is an extremely useful technique for the investigation of the interaction between humic acids and cations. Drozdova and Emelyanova (1960), for example, used this technique to study the interaction of copper with humic acids. In the investigations reported in this section, electrophoresis was used to examine the interaction between THA-1 and THA-4 and the cations Ag^{+1}, Co^{+2}, Cu^{+2}, Ni^{+2}, Pb^{+2} and Zn^{+2}. The electrophoresis was carried out on 100 mm x 20 mm cellulose acetate membranes with a borate electrolyte consisting of 0.02 M $Na_2B_4O_7$, adjusted to pH = 8.6 with H_3BO_3.

A counter current technique was used in which the humic acids were applied as spots (20 µg THA-1 or THA-4) near the cathodic end of the membrane with excess cations being applied on the anodic side of this location. A potential of 200 V was applied causing the humic acids and cations to migrate through one another as the former moved to the anode and the latter to the cathode. Approximately one hour was required for the humic acids to migrate about 60 mm, at which point electrophoresis was discontinued. All cations yielded the same pattern of migration and the appearance of the membranes before and after electrophoresis is illustrated in Figure 22.
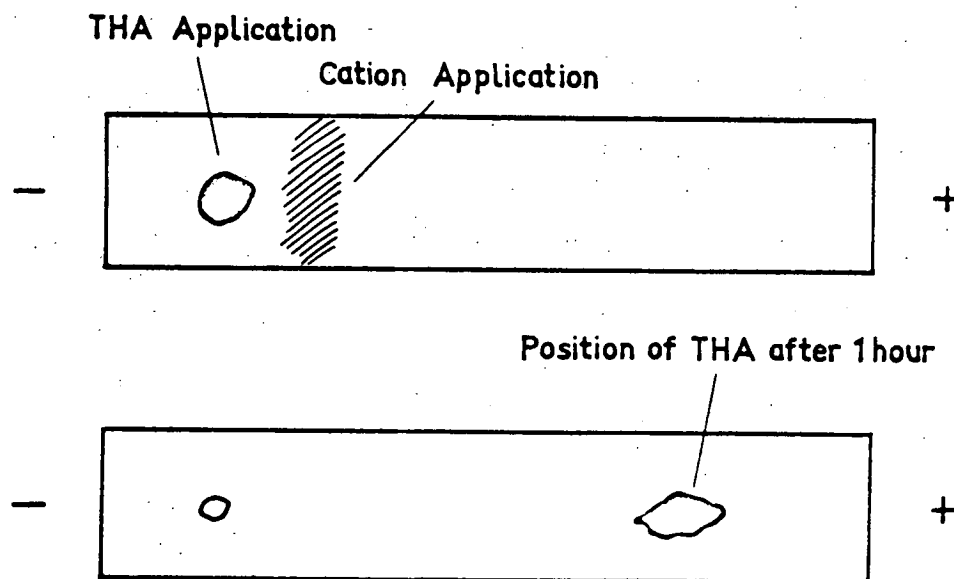
Figure 22. Appearance of membranes before and after electrophoresis of humic acids and cations.

The spots of humic acids were cut out of the membranes after each run and placed in 0.5 ml of ammoniacal EDTA. This dissolved the humic acids and the solutions were analysed for metal content by an atomic absorption carbon cup technique (AACC). The metals applied as cations were all found to be associated with the humic acids at the anodic extremity of the membranes. The semi-quantitative data obtained by the AACC analyses are given in Table 15. It is thus apparent that substantial amounts of metal formed complexes of sufficiently high stability to resist breakdown under an applied potential of 200 V.

Table 15. *SEMI-QUANTITATIVE ANALYTICAL RESULTS FOR METALS ASSOCIATED WITH HUMIC ACIDS ON ELECTROPHORESIS MEMBRANES.*

Metal	ng metal associated with 20 µg of	
	THA-1	THA-4
Cobalt	250	200
Copper	1350	1050
Nickel	300	300
Lead	1650	1200
Silver	450	400
Zinc	400	300

7.3 Infra-red spectra of associations of cations with humic acids

The infra-red spectra of the Tasmanian humic acid samples were illustrated in Chapter 3 (fig. 8). Amongst the absorption bands recognised was one in the frequency range 1725 to 1640 cm^{-1} which was in part due to C=O stretching of carboxylic acids. The effects of interactions of cations with humic acids on this absorption band were investigated by recording infra-red spectra of the associations of Cu^{+2}, Pb^{+2} and Zn^{+2} with THA-1 and THA-4.

The metal humates were prepared by adding 2 ml of a 50 μmole/ml solution of the required cation to 5 ml of a 1% solution of the humic acids. The excess cations were removed by dialysis and the humates dried at 40°C. The samples were mixed with KBr in the proportion of 1:400 and pelletised. The infra-red spectra were recorded against a blank of KBr and these are shown in Figure 23. These spectra are seen to exhibit similar features. For all the metal humates, the absorption in the range 1725 to 1640 cm^{-1} has decreased relative to its extent in the pure humic acids (*e.g.* THA-1/Cu compared with THA-1). This is apparently due to increased ionisation of COOH with the formation of metal humates. In addition the spectra for the humates show a slight increase in absorption at a frequency of about 1400 cm^{-1} which, according to Wagner and Stevenson (1965), is due to the formation of salts of carboxylic acids. The infra-red spectra thus clearly show the involvement of carboxylic acid groups in the interaction between humic acids and cations.

7.4 *Metal humates as mobile systems in the weathering cycle*

The concept that metal humates, other than those formed with alkali metals, are of low solubility originated with early studies, such as those of Odén (1919), which remains the basis of classification of these substances. This low solubility is with respect to distilled H_2O, and the actual values found are highly dependent on the means of preparation of the humates and time of ageing of the products (Kononova, 1966). In the natural environment of humid climates, rainfall supplies water to a soil layer in which bacterial action is continually producing humic substances. These substances along with numerous other biochemicals produce a solvent which on interaction with mineral surfaces forms metal humates.
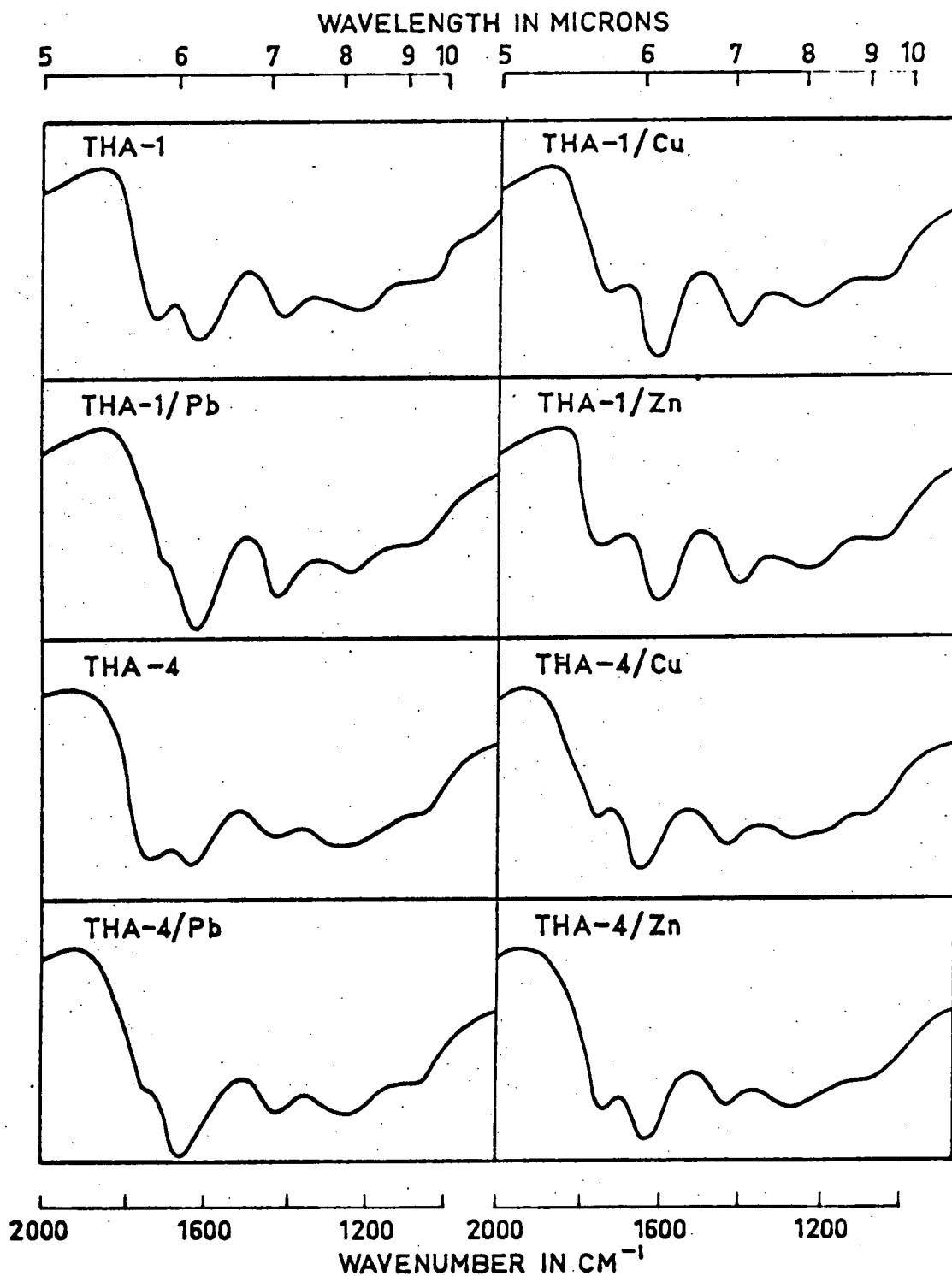
Figure 23. *Infra-red spectra of humic acids THA-1 and THA-4 and their associations with Cu^{+2}, Pb^{+2} and Zn^{+2}.*

Whether or not these humates are immobile is largely dependent on their subsequent history. In the humid climates they must be frequently in contact with recently generated solvents from the organic layers of the soil. Experiments were carried out to examine the behaviour of metal humates when exposed to humic acid solutions. The metal humates were prepared by mixing 5 ml of 0.5% solutions of THA-1 and THA-4 (25 mg) with 5 ml of 0.1 M solutions of Al^{+3}, Ca^{+2}, Co^{+2}, Cu^{+2}, Fe^{+3}, Mg^{+2}, Mn^{+2}, Ni^{+2}, Pb^{+2} and Zn^{+2}. The coagulated humates were separated by centrifuging, mixed with macerated filter paper and dried for three days at 30°C. The dried pads of humates were confined between 2 cm pads of compacted macerated filter paper, in 5 cm x 2 cm glass columns with bases of sintered glass.

The excess inorganic salts were washed from the column with up to 100 ml of distilled H_2O. In several cases, coloration of the eluant indicated that the humates had commenced to move and where this occurred washing was discontinued. Each humate was leached with ten successive 10 ml aliquots of distilled H_2O, followed by a like series of 500 mg/l solutions of THA-1 or THA-4. These were analysed for metal content by AAS. Where the distilled H_2O eluants showed some colour they were combined and the average content of humic acids was determined spectrophotometrically.

The results of the experiments are presented diagramatically in Figure 24 and the analytical data on which this is based are given in Appendix 4. All humates, excepting that of Al^{+3}, exhibited similar behaviour and the leaching paths fall within the shaded areas of the diagrams, which also record the identities of the cations providing the extremes of the leaching fields. The humates all display low mobility in distilled H_2O but become highly mobile in the presence of humic acids. The humates of aluminium are the exception as these remain of low mobility in both distilled H_2O and solutions of humic acids. The humates of Ca^{+2}, Co^{+2}, Mg^{+2}, Mn^{+2}

and Ni^{+2} display some mobility in distilled H_2O and as can be seen from Figure 25 the metals in solution show an approximate correlation with the amount of humic acids present. The steeper gradient in the case of THA-4 indicates a higher mobility for humates formed with this sample. This is consistent with the relative mobilities of THA-1 and THA-4 which was demonstrated by paper chromatography as illustrated in Figure 7 of Chapter 3. The results presented here are in general agreement with earlier studies with 1 g/l solutions of THA-1 (Baker, 1973) except for nickel humates. In the earlier studies these were found to have a very high mobility in distilled H_2O. As this feature has not been reproduced, the earlier result must be considered in error, due probably to a breakdown in the physical characteristics of the elution system.

Since solutions of humic acids have considerable effect on the mobility of humates a study was made of cations absorbed on Fe_2O_3 and montmorillonite. Solutions of 0.1 M Co^{+2}, Cu^{+2}, Ni^{+2}, Pb^{+2} and Zn^{+2} were shaken with 25 mg of Fe_2O_3 or montmorillonite for one hour, after which the solids were concentrated by centrifuging, washed several times with distilled H_2O and subjected to elution studies by the same procedures as were used for the humates. The results are presented in Figures 26 and 27 and the analytical data in Appendix 3. It can be seen from these diagrams that, whereas the adsorbed cations are relatively immobile in the presence of distilled H_2O, they are rapidly mobilised by the humic acid solutions.

7.5 *Reaction kinetic study of the activity of THA-1*

There do not appear to be any reports of studies of the reaction kinetics of the interaction between humic acids and minerals. In a series of papers Huang and Keller (1970, 1971, 1972) investigated the kinetics of reactions between a number of silicates and simple organic acids. They found that the dissolution of aluminium, potassium and magnesium followed a first order reaction whereas the removal of silicon and iron appeared to be diffusion controlled.
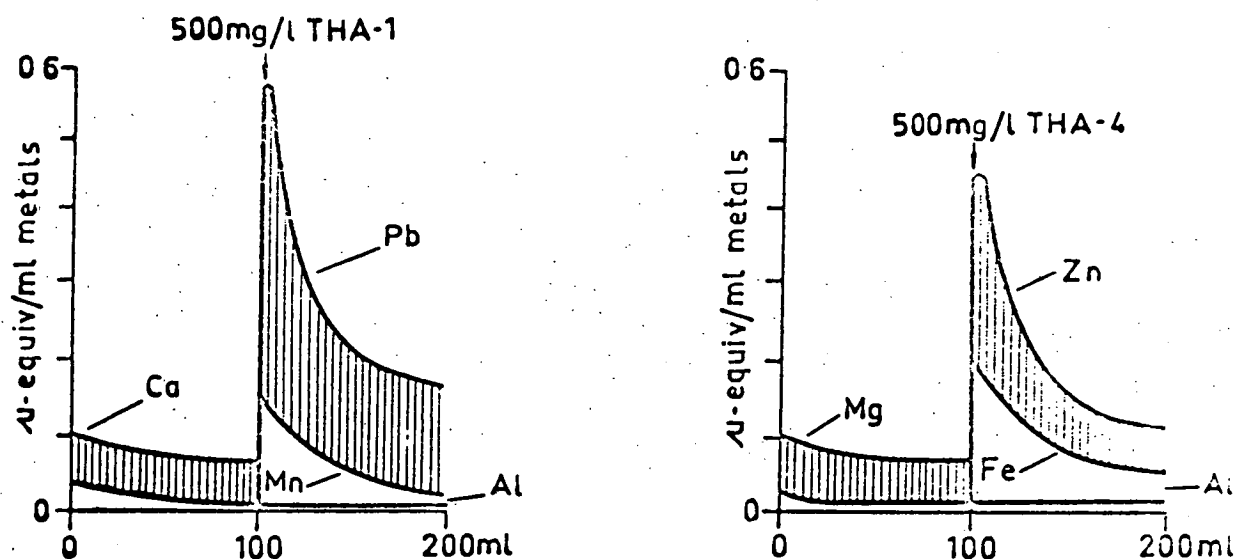
Figure 24. *Leaching of Al, Ca, Co, Cu, Fe, Mg, Mn, Ni, Pb and Zn precipitated with 25 mg of THA-1 and THA-4 by 100 ml H_2O followed by 100 ml of 500 mg/l solutions of THA-1 and THA-4. Elements indicated show maximum and minimum mobilities in H_2O and humic acids. Note relative immobility of Al.*
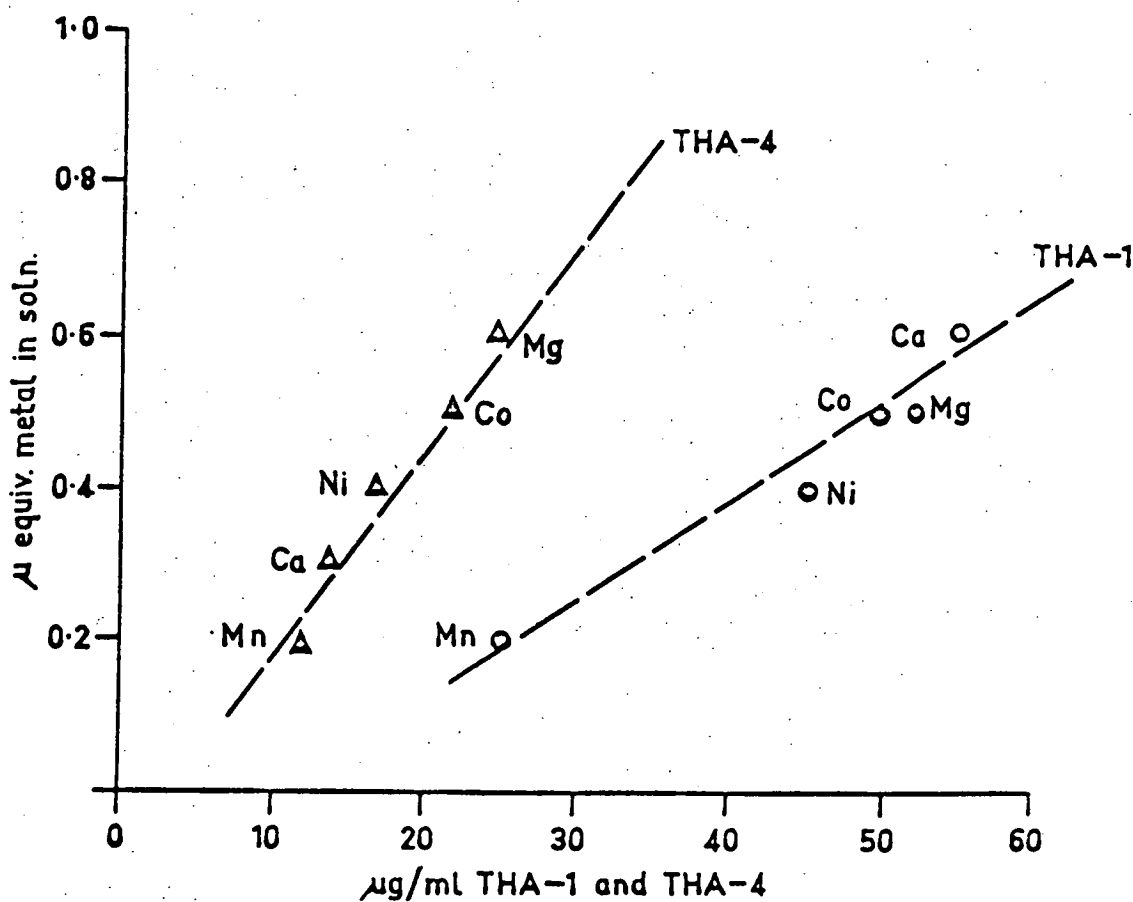
Figure 25. *Correlation of metal humates mobilised in distilled H_2O with the amount of humic acids present.*
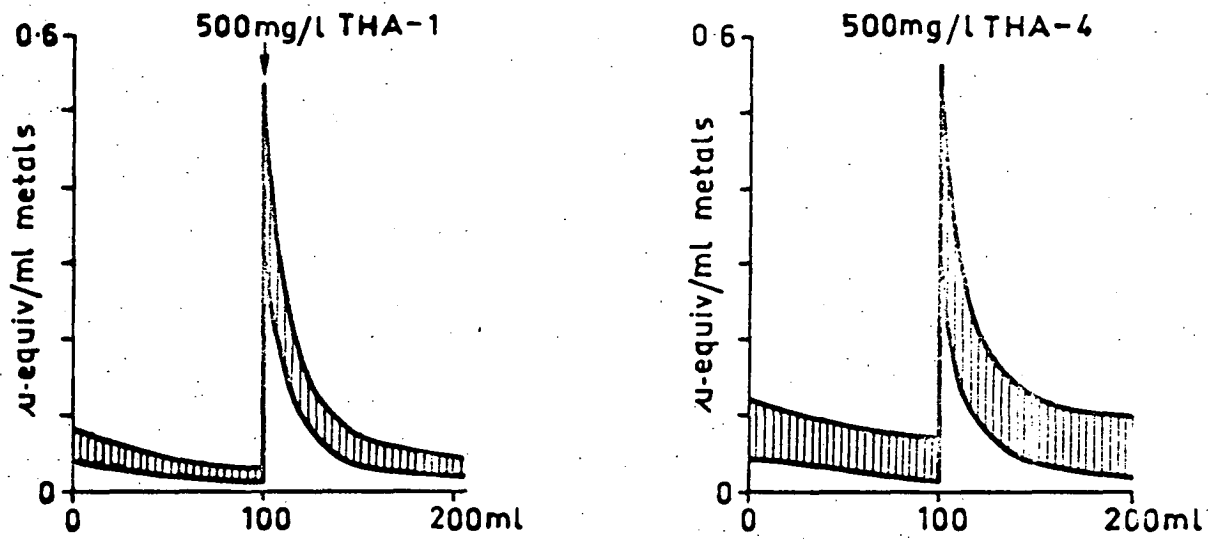
Figure 26. *Leaching of Co, Cu, Ni, Pb and Zn absorbed on 25 mg*
Fe_2O_3 by H_2O and 500 mg/l solutions of THA-1 and THA-4.
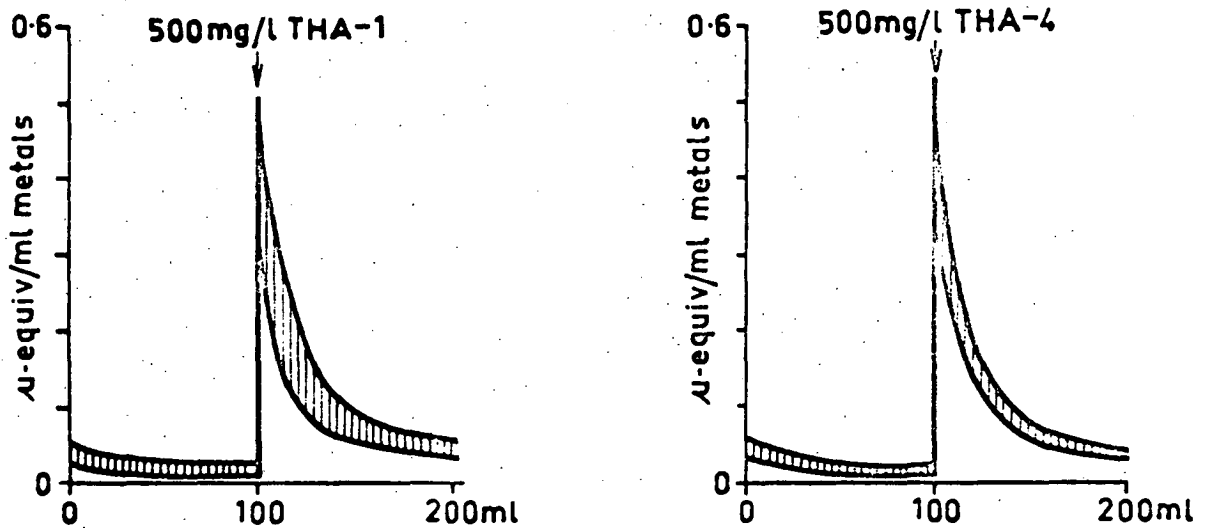
Figure 27. *Leaching of Co, Cu, Ni, Pb and Zn absorbed on 25 mg*
montmorillonite by H_2O and 500 mg/l solutions of
THA-1 and THA-4.

In this study, investigations were undertaken to find out whether or not the rapid reactions of many minerals with humic acids, reported in Chapter 4, were of first order. In a first order reaction the rate of change in concentration is directly proportional to the concentration. Thus if 'a' is the initial concentration, and 'a - x' that after a lapse of time 't', the instantaneous rate of reaction is given by:

$$- \frac{d \, (a - x)}{dt} = \frac{dx}{dt} = k \, (a - x) \quad \ldots (1)$$

where 'k' is the velocity constant. Integration of (1) to evaluate 'k' yields:

$$k = \frac{1}{t} \ln \frac{a}{a - x} \quad \ldots (2)$$

If the time $t_{0.5}$ is taken as that required for the initial concentration to be reduced by half, in which case $x = \frac{a}{2}$ then substitution in (2) results in:

$$t_{0.5} = \frac{\ln 2}{k} \quad \ldots (3)$$

Hence the important feature of a first order reaction is that the time required to complete a definite proportion is independent of the initial concentration.

Thus a satisfactory test for a first order reaction would be to monitor its progress after starting with two different initial concentrations. This was applied to reactions of metallic lead, cerussite and anglesite with 500 mg/l and 1 g/l solutions of THA-1. The depletion of the humic acid was monitored by determining the amount of lead entering solution as a result of reaction. The experiments were carried out with an arrangement similar to that in Figure 9 of Chapter 4. The outer vessel was increased to 200 ml capacity to enable use of 100 ml volumes of the humic acids, and was placed over a magnetic stirrer to enable continuous agitation

of the solvent phase. The extraction of lead from the minerals was monitored by taking 1 ml aliquots for analysis by AAS over a twelve hour period. During the first hour aliquots were taken every ten minutes and after this period the sampling interval was first increased to thirty minutes and finally to four hours. The results are given in Tables 16, 17 and 18 and the graphs drawn from these appear in Figures 28, 29 and 30.

It is evident from Figures 28, 29 and 30 that there is rapid depletion of the humic acids with a resultant decrease in the rate

Table 16. REACTION KINETIC STUDY OF THE DISSOLUTION OF METALLIC LEAD BY 1 g/l AND 500 mg/l SOLUTIONS OF THA-1

Time (min)	500 mg/l THA-1		1 g/l THA-1	
	μg/ml Pb in aliquot	Total Pb extracted (mg)	μg/ml Pb in aliquot	Total Pb extracted (mg)
10	96	9.6	114	11.4
20	134	13.4	184	18.3
30	166	16.5	244	24.2
40	188	18.6	290	28.7
50	207	20.5	328	32.3
60	224	22.1	375	36.8
90	252	24.7	437	42.6
120	276	26.9	472	49.0
150	298	29.0	506	49.0
180	314	30.4	530	51.2
210	326	3.15	548	52.8
240	344	33.1	564	54.2
300	352	33.8	570	54.8
360	364	34.5	576	55.3
480	370	35.0	582	55.8
720	368	35.5	576	55.6
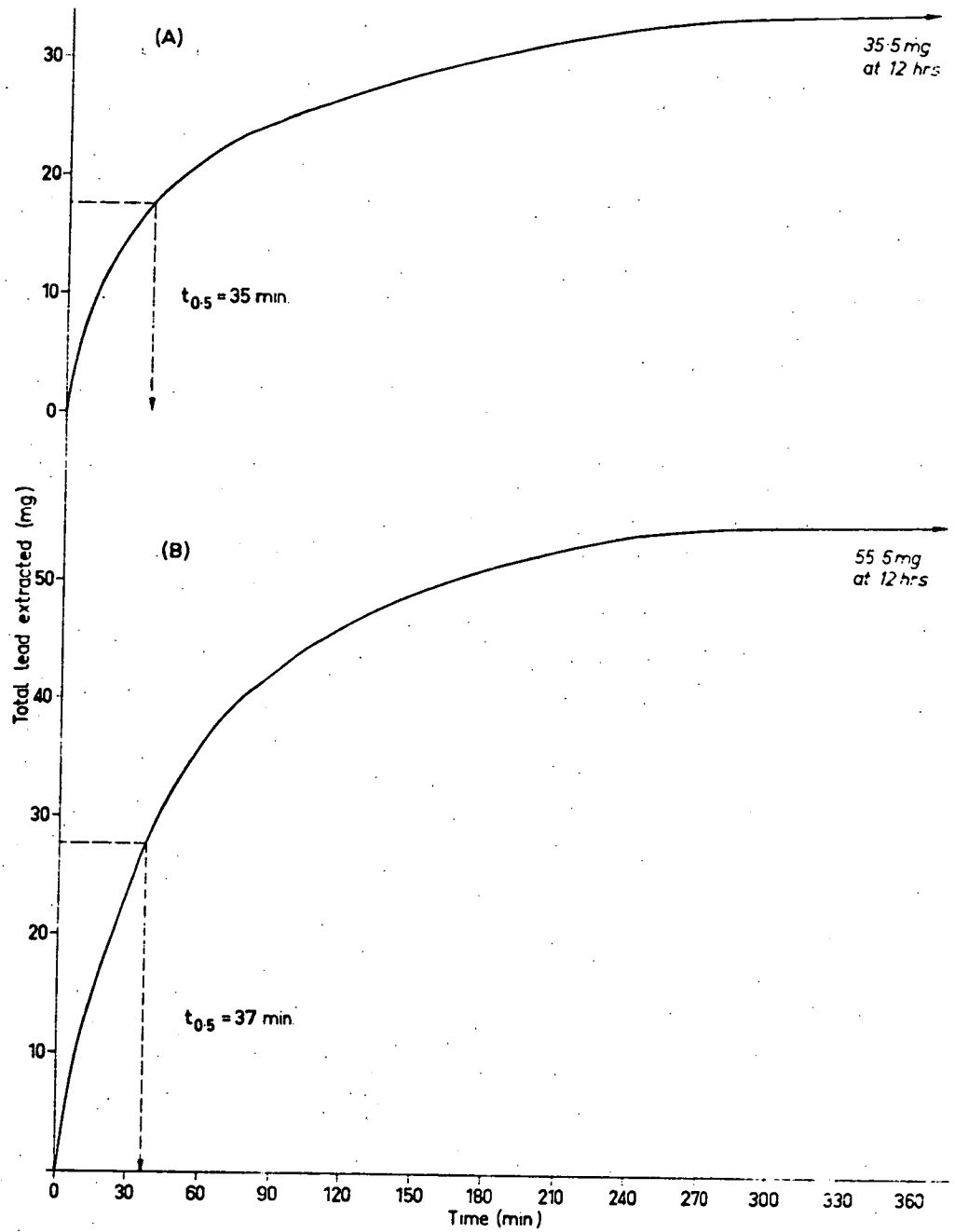
Figure 28.   *Reaction rate curves for dissolution of metallic lead by solutions of (A) 500 mg/l THA-1 and (B) 1 g/l THA-1.*

Table 17. REACTION KINETIC STUDY OF THE DISSOLUTION OF CERUSSITE
BY 1 g/l AND 500 mg/l SOLUTIONS OF THA-1

Time (min)	500 mg/l THA-1		1 g/l THA-1	
	μg/ml Pb in aliquot	Total Pb extracted (mg)	μg/ml Pb in aliquot	Total Pb extracted (mg)
10	42	4.2	142	14.2
20	84	8.4	208	20.7
30	131	13.0	264	26.2
40	164	16.2	292	28.9
50	178	17.5	312	30.9
60	185	18.2	334	32.9
90	204	20.0	375	36.3
120	212	20.7	394	38.6
150	220	21.4	405	39.6
180	220	21.4	420	40.9
210	228	22.2	432	42.0
240	231	22.4	450	43.6
300	230	22.3	462	45.2
360	238	23.0	470	45.4
480	240	23.2	478	46.1
720	238	23.0	474	45.7

of the reaction. In theory the reactions should never end, but become

asymptotic to the time axis, although for all practical purposes

the humic acids are almost totally depleted after twelve hours. From

the amount of lead extracted at this time the quantity half this

in value can be estimated, and from the graphs the related $t_{0.5}$ value

can be obtained. These values are given in Table 19. It can be

seen from the close agreement between pairs of $t_{0.5}$ values for the

systems investigated, that the reaction of humic acids with minerals
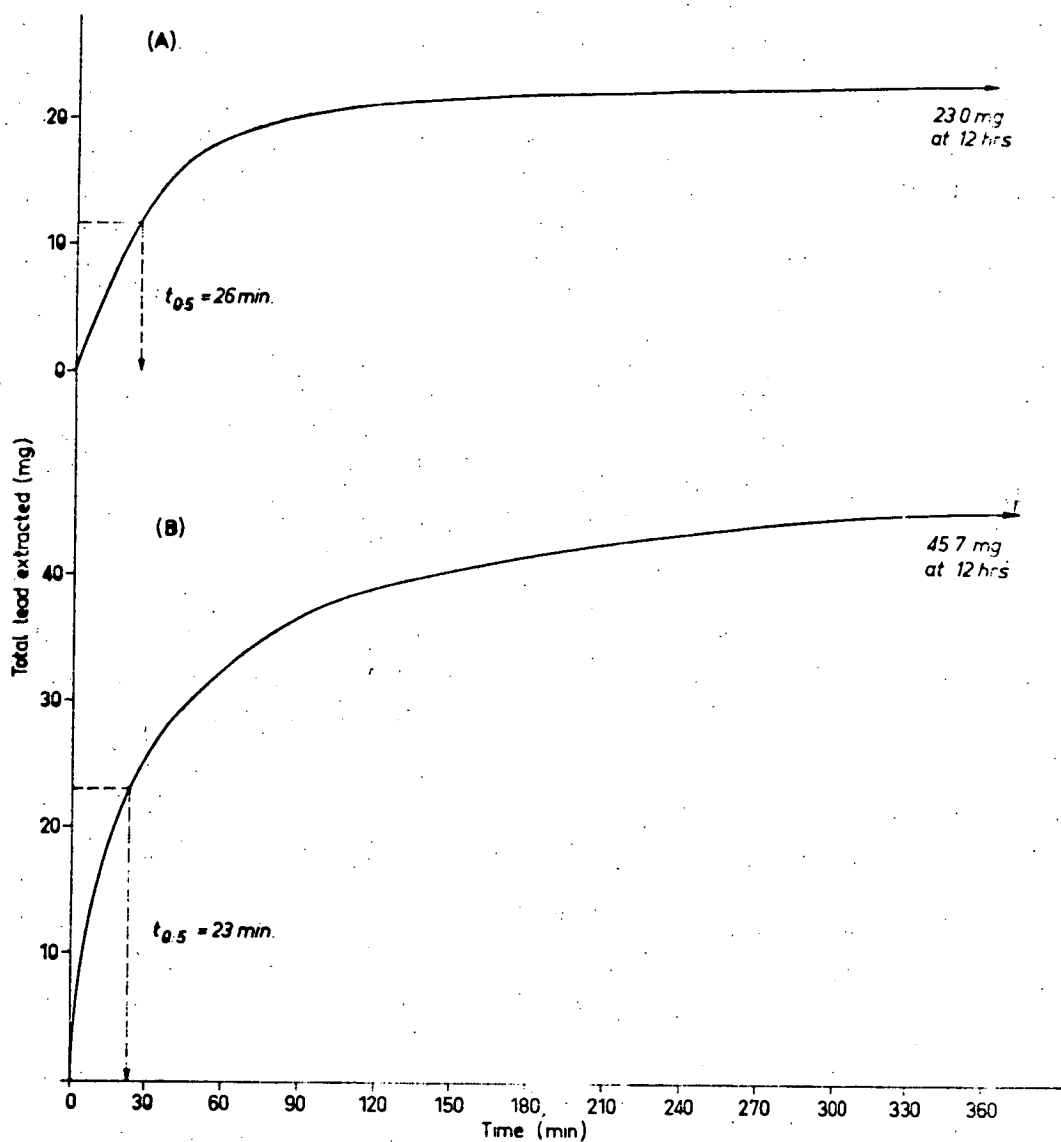
Figure 29.   Reaction rate curves for dissolution of cerussite
              by solutions of (A) 500 mg/l THA-1 and (B) 1 g/l
              THA-1.

Table 18. *REACTION KINETIC STUDY OF THE DISSOLUTION OF ANGLESITE BY 1 g/l AND 500 mg/l SOLUTIONS OF THA-1*

Time (min)	500 mg/l THA-1		1 g/l THA-1	
	µg/ml Pb in aliquot	Total Pb extracted (mg)	µg/ml Pb in aliquot	Total Pb extracted (mg)
10	17	1.7	37	3.7
20	34	3.4	64	6.4
30	47	4.6	80	7.9
40	56	5.4	94	9.3
50	62	6.0	105	10.4
60	71	6.8	117	11.5
90	82	8.0	137	13.4
120	88	8.6	155	15.0
150	98	9.1	166	16.1
180	101	9.2	173	16.7
210	110	10.0	184	17.7
240	114	10.2	195	18.7
300	128	11.4	214	20.3
360	134	11.8	220	20.8
480	147	12.8	236	22.2
720	149	12.8	240	22.6

appears to be of first order. This is an important result in that it validates the extrapolation of laboratory experiments, which are of necessity carried out with high concentrations of humic acids, to the natural environment where solvents are of lower concentration.
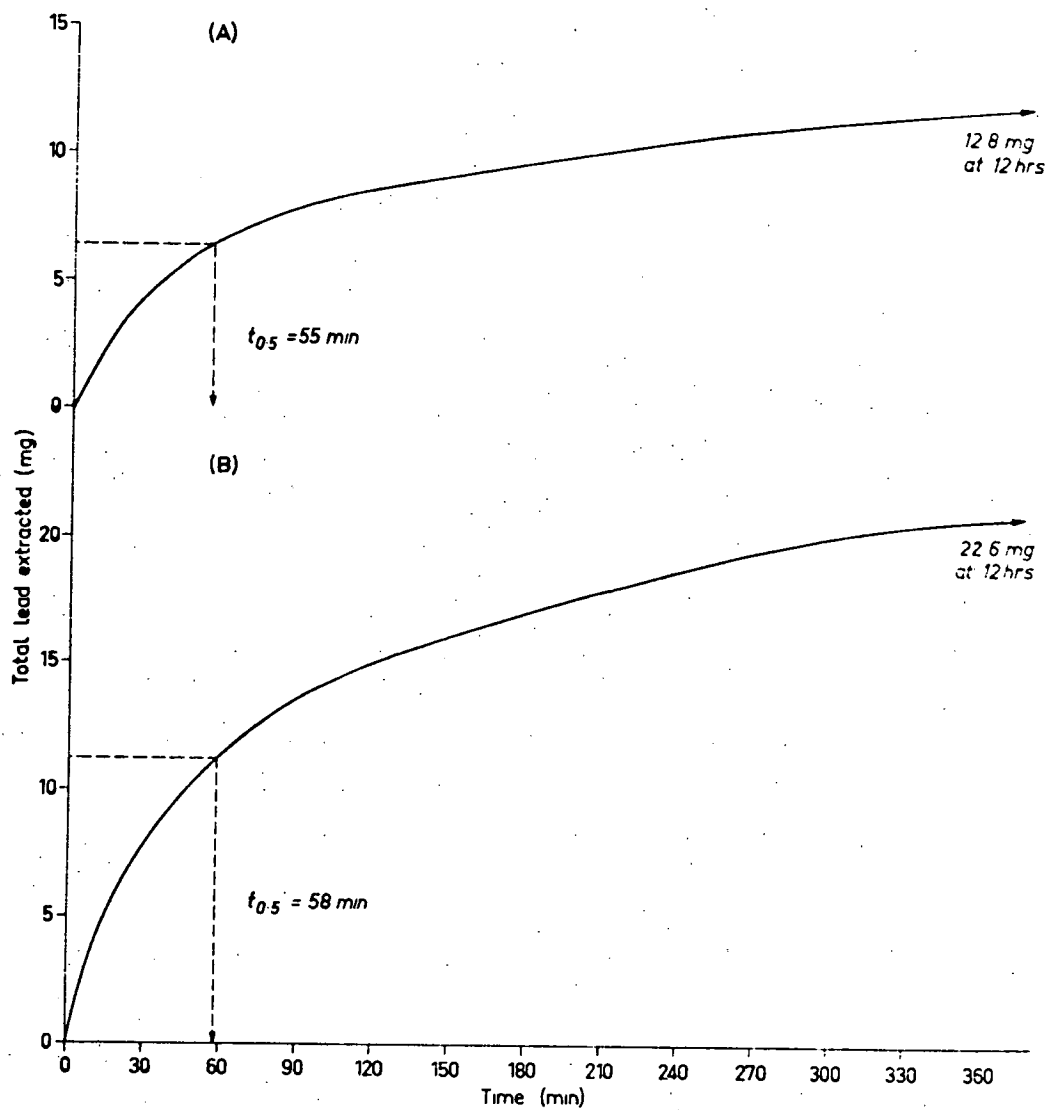
Figure 30.   *Reaction rate curves for dissolution of anglesite by solutions of (A) 500 mg/l THA-1 and (B) 1 g/l THA-1.*

Table 19. *Reaction kinetic data for the dissolution of lead*
minerals by THA-1

System	Pb extracted at completion of reaction (mg)	Half total extraction value (mg)	$t_{0.5}$ value (min)
Metallic Pb - 500 mg/l THA-1	35.5	17.8	35
Metallic Pb - 1 g/l THA-1	55.6	27.8	37
Cerussite - 500 mg/l THA-1	23.0	11.5	26
Cerussite - 1 g/l THA-1	45.7	22.9	23
Anglesite - 500 mg/l THA-1	12.8	6.4	55
Anglesite - 1 g/l THA-1	22.6	11.3	58

7.6 Stability of the metal humates

In simple cases of metal complexation where the ratio of ligand.

(L) to metal (M) is 1:1 the equilibrium equation is:
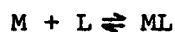
$$M + L \rightleftharpoons ML$$

and the equilibrium constant is given by:

$$K = \frac{(ML)}{(M)(L)}$$

In reactions involving complexation, the equilibrium constant is

referred as the stability constant since it is a measure of the

stability of the complex. Whilst stability constants may be

determined for well defined chemical systems, the very nature of

humic acids renders impossible the absolute determination of the

stability of metal humates. Mellor and Maley (1947, 1948) established

that the stability of M^{+2} complexes follows the order Pd>Cu>Ni>Co>Zn>

Cd>Fe>Mn>Mg irrespective of the nature of the ligand involved. This

work was extended by Irving and Williams (1948) and the series given

above is identified by the use of their names.

Stability constant values for the metal complexes formed by

the action of humic substances have been calculated in a number of

investigations. Beckwith (1959) and Kanna and Stevenson (1962)

concluded that the stability of the metal humates followed the

Irving-Williams series. Schnitzer and Skinner (1966, 1967) found

that for metal fulvates the order of stabilities at pH = 5 was:

Cu>Pb>Fe>Ni>Mn = Co>Ca>Zn>Mg. They commented that this was at

variance with the Irving-Williams series, particularly with reference

to the high stability of the fulvates of iron relative to those of

zinc. Guy and Chakrabarti (1976) found an order of Pb>Cu>Cd>Zn

for complexes of both humic and tannic acids.

The problem with stability constant data determined for the

metal complexes of humic substances is that they are based on two

averaging processes. Firstly, an average molecular weight is assigned

and, as was noted in Chapter 1, the range is large and the averaging

procedure of dubious validity. Secondly, the humic substances present

an array of functional groups, each with their own particular

stability characteristics, which are assigned a value of average

performance. Considerable effort has been expended on the development

of an acceptable concept of average stability constants for humic

substances (e.g. MacCarthy, 1977). The fact remains, however,

that quite different distributions of stability constants could

yield the same average value. Furthermore, since the molecular

weight of the humic substances is not an accurately known value,

the numbers which result from the various calculations are not

referable to any standard physiochemical scale. Despite these

limitations the concept of average stability constants find wide

usage within the confines of soil science. It is of lesser value

in the more general field of geochemistry.

These limitations suggest that it would be useful to have

some measure, in absolute terms, of the range in stability of the

various complexing sites of humic acids. In this study a completely

empirical approach has been made to this problem and to date only

preliminary experiments have been carried out. Copper humates were

formed with THA-1 and THA-4 and the excess metal removed by dialysis.

Analysis of the humates revealed that the copper content of the THA-1

and THA-4 preparations were respectively 2.84 and 2.46 µeq/100 mg.

The humates were then shaken with a series of 0.05 M solutions of

complexing agents which formed copper complexes of varying stability.

The copper released was monitored by introducing dialysis bags

containing distilled H_2O into the mixed copper humate and complexing

agent systems. After three days the copper displaced from the humic

acids was analysed by AAS and the results are given in Table 20.

The results indicate that this approach may prove useful in

considerations of the fate of metal humates in the geochemical cycle.

On the basis of the limited data available, the copper humates of

THA-1 and THA-4 appear to exhibit similar patterns of stability.

The complexing agents used were restricted by ready availability at

the time of conducting the experiments. Further studies with a

better graded series are desirable, particularly in the range of

$Log_{10}K_1$ between 3.4 and 4.2 where there is a marked increased in

the copper released from the humates. It would also be desirable

to check that the literature values for the stability constants of

the selected complexing agents, do not vary under the conditions

of experimentation used in these preliminary studies. From Table 1

it appears that most of the copper held by THA-1 and THA-4 forms

complexes which have a range of stability equivalent to $\text{Log}_{10} K_1$

values of 4 to 6. About 15% of the copper is bound with sufficient

strength to require the action of EDTA for removal. This is in

keeping with the comments of Nissenbaum and Swaine (1976) who found

trace metals to be very tenaciously held by marine humic acids.

Table 20. RELEASE OF COPPER FROM THA-1 AND THA-4 HUMATES BY 0.05 M
COMPLEXING AGENTS

Complexing agent	Stability constant ($\text{Log}_{10}K_1$)	THA-4		THA-1	
		Cu released (μ eq)	Total Cu (%)	Cu released (μ eq)	Total Cu (%)
Succinic acid	2.93	0.20	8	0.18	6
Maleic acid	3.4	0.22	9	0.26	9
Acetylactone	4.2	1.04	44	1.18	42
Malonic acid	5.55	1.72	72	2.12	76
Citric acid	5.9	2.00	84	2.36	85
E.D.T.A.	18.3	2.38	97	2.78	98

CHAPTER 8

THE ROLE OF HUMIC ACIDS IN THE TRANSPORT OF GOLD

The migration of gold in the weathering cycle has been the subject of many investigations. Conflicting views and experimental evidence have been advanced favouring both inorganic and organic processes for the solution and transport of gold Stokes (1906) and others studied the solution of gold by inorganic solvents, such as $Fe_2(SO_4)_3$, which may occur in nature and found that substantial solution occurred only in the presence of Cl^-. Krauskopf (1951, 1967) presented experimental evidence and thermodynamic data for the dissolution of gold as $AuCl_4^-$. Lakin *et al.* (1974) have suggested that HCN resulting from hydrolysis of naturally occurring cyanoglycosides, which are present in many plants, could be responsible for the mobility of gold in soils.

As noted in Chapter 2 (section 2.4) Julien (1879) made a generalised proposal that humic acids were active in the precipitation of gold in alluvial deposits. Freise (1931) drew attention to the fact that some of the gold of Brazilian alluvial deposits was extremely fine-grained and of high purity, in contrast with detrital gold which contained copper. The high purity gold often carried a brown to black coating which was found to be iron humates. This 'black gold' as it has been named by prospectors, occurs in many alluvial gold deposits and has been observed by the writer from the Lisle and Jane River gold deposits in Tasmania. Ong and Swanson (1969) have noted the occurrence of carbonaceous matter with gold in sedimentary rocks from several regions including the Witwatersrand in South Africa and Hallbauer (1975) has presented a comprehensive review of the association of carbon with the former deposits. It is possible that such carbonaceous matter originated as humates.

Freise (1931) also presented experimental evidence for the solubility of gold in humic acids and Baker (1973) confirmed this. The theoretical plausibility of the formation of gold complexes with humic acids was established by Shcherbina (1956). Contrary views have been expressed by Fetzer (1934, 1946) and Ong and Swanson (1969). The latter investigators proposed that gold is transported as a colloid, in a system in which humic acid acts as a reductor and as a protective colloid. Krauskopf (1974) accepted this model but also suggested that gold is mobilised as $AuCl_4^-$.

Modern reviews of the transportation of gold, such as that by Krauskopf (1974), do not mention any evidence of the potential of humic acids to form complexes with gold. Such omissions have prompted a further and more thorough examination of the interaction of gold with humic acids, involving solution, electrophoresis, polarographic, solvent extraction and X-ray diffraction investigations.

8.1 *Solubility of gold in humic acids*

The potential of humic acids to dissolve gold was investigated in the following manner. Since it was anticipated that several weeks of reaction would be required to bring detectable gold into solution, the experimental arrangement consisted of six test tubes attached to a horizontal shaft which could be rotated at 100 rph.

With this arrangement 2 g of gold having a particle size range of 0.07 mm to 0.15 mm were placed in each of the six test tubes, and allowed to react in duplicate with 20 ml of distilled H_2O, and 500 mg/l solutions of THA-1 and THA-4 for a period of 50 days. The initial pH and Eh values of the solutions of the humic acids were 3.7 and +340 mV for THA-1 and 3.4 and +330 mV for THA-4. These values are compatible with those of natural solutions between rain water and bog waters, as given by Garrels (1960), and are probably representative of many soil waters.

At the completion of the 50 days reaction period the solutions were filtered through Whatman No. 42 paper and analysed by the AAAC technique which allowed a precision of about ± 10 ng Au/ml. The results, given in Table 21 show average yields of 10, 190 and 330 ng Au/ml for distilled H_2O, THA-1 and THA-4 respectively, which indicates considerable mobilisation of gold in the presence of humic acids. There was no significant change in the pH and Eh values of the humic acid solutions as a result of their reaction with gold.

Table 21.   DISSOLUTION OF Au (ng/ml) BY H_2O AT ATMOSPHERIC CO_2 PRESSURE AND HUMIC ACID SOLUTIONS (THA-1 AND THA-4) IN 50 DAYS

Run No.	H_2O/CO_2	0.05% THA-1	0.05% THA-4
1	8	200	300
2	11	170	360
3	10	210	320
Average	10	190	330

8.2   Electrophoresis study of gold mobility

As was seen in Chapter 7 (section 7.2) electrophoresis can be used to study complexation of cations by humic acids. To apply the technique in this study it was necessary to impregnate the electrophoresis membranes with a confined spot of gold. This was achieved by applying, in succession, 5 µl drops of solutions of 1% $SnCl_2$ and 1 mg Au/ml as $HAuCl_4$ (5 µg Au) at equivalent points of four 100 mm x 20 mm membrane strips. After excess reagents were leached away by leaving the membranes in a large volume of distilled H_2O for 24 hours there remained spots of precipitated gold. Blank membranes were treated in the same manner, with the omission of the $HAuCl_4$ application. Before use, the membranes were soaked in a borate buffer of 0.02 M $Na_2B_4O_7$ adjusted to pH 8.6 with H_3BO_3. A 1% THA-1 solution (pH 3.2)

was applied as a 5 µl drop (50 µg THA-1) on the cathodic side

of the gold spot on two of the membranes and in an equivalent

position on the two blanks. An electrophoresis cell was set up with

the borate buffer and the membranes carrying gold, THA-1 and gold

with THA-1 were subjected to electrophoresis at a potential of 300 V

for 15 minutes. The runs were made in duplicate. One set of

membranes was used for analytical purposes whilst the other was kept

as a record of the electrophoretograms which are illustrated in

Figure 31.

The comparative gold contents of the humic acid fronts and the

equivalent site for the gold run were determined by AACC analysis

of 1 mm sections of the membranes. The analyses reveal that the front
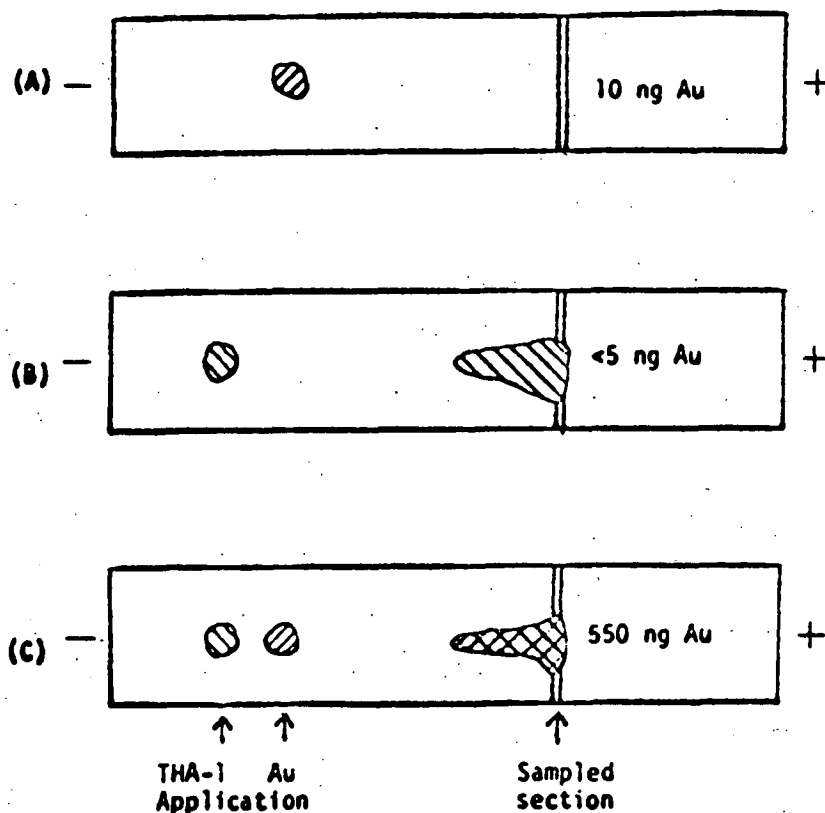
Figure 31. *Electrophoretograms of (A) Au, (B) THA-1 and (C) Au
with THA-1. Au contents of sampled membrane sections
as indicated.*

on the gold with THA-1 membrane contains 550 ng Au, which is far in

excess of the 10 ng Au in the equivalent position of the membrane

carrying gold alone. A small amount of gold (<5 ng), which is near

the detection limit, was found in the blank membrane and this is

believed to be a contaminant acquired during the leaching of excess

reagents from the membranes. The high content of gold in the sample

from the membrane carrying gold with THA-1 suggests that the metal

has been mobilised as complexes with the humic acids.

8.3 Polarographic investigations of the association of gold with humic acids

In order to study the polarographic reduction of Au^{+3} a

supporting electrolyte of 1 M NaOH appeared to be the only choice

which offered a well developed polarographic wave for gold, and also

ensured solubility of the humic acids. Using this system, polarograms

were recorded for the reduction of 10 μg Au^{+3} /ml in the absence and

presence of 50 mg THA-1 by means of pulsed DC polarography. The $Au(OH)_4^-$

complex was stable in NaOH for several hours but eventually the

formation of colloidal gold was indicated by the appearance of a

red-blue colour in the solution. For this reason polarograms were

recorded as soon as the solutions had been prepared and flushed with N_2

and again after a period of 24 hours. The resulting polarograms

are shown in Figure 32.

In Figure 32A the polarographic reduction of Au^{+3} is seen to

occur with a half-wave potential of -0.53 V (vs SCE) and a diffusion

current of 8.2 μA. The residual current in this case is near zero.

Reduction in the presence of THA-1 is shown in Figure 32B which

reveals that for this system the half-wave potential has moved to
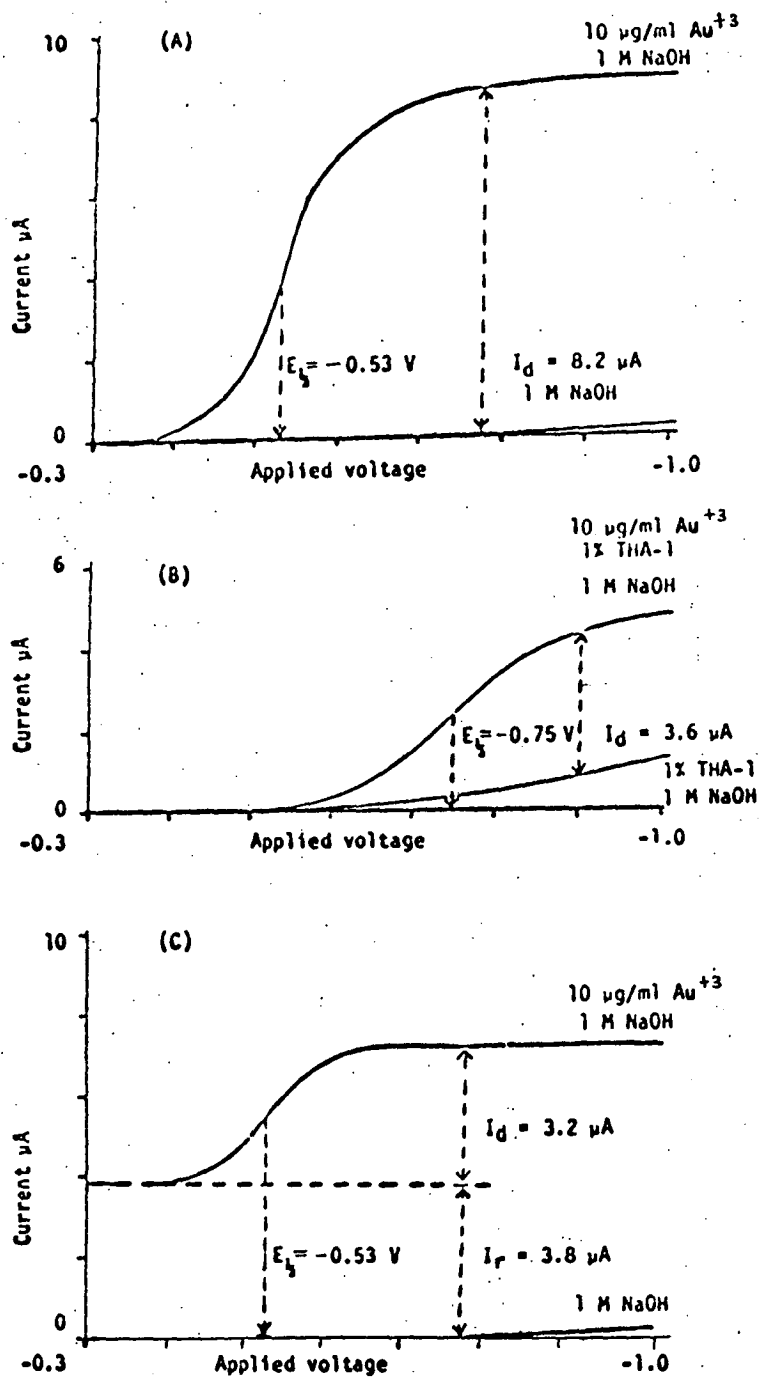
Figure 32.   Polarograms of (A) 10 µg/ml Au^{+3} in 1 M NaOH
(B) as for (A) with addition of THA-1 and (C)
repeat of (A) after lapse of 24 hours.

-0.75 V and the diffusion current has decreased to 3.6 μA. There is a small residual current due to the electrolytic properties of the humic acids. This change in wave characteristics is clear evidence of the complexation of gold by humic acids. The large shift of the half-wave potential of -0.22 V in the presence of THA-1 indicates that the average stability constant of the complexes of gold with the humic acids is greater than that of $Au(OH)_4$. Figure 32C shows the results of repeating the polarographic reduction of Au^{+3} in NaOH after 24 hours. The half-wave potential remains at -0.53 V although the presence of colloidal gold has caused a sharp increase in the residual current. Since the concentration of Au^{+3} has been decreased by the formation of colloidal gold, the diffusion current has fallen to 3.2 μA. The polarogram of Au^{+3} in NaOH with THA-1, repeated after 24 hours, was found to be identical with Figure 32B. Thus in the presence of THA-1, complexes with gold have formed which remain stable and prevent the formation of colloidal gold.

8.4 Solvent extraction studies of gold complexes

Shcherbina (1956) suggested that the complexes of gold with humic acids are stronger than $AuCl_4^-$ and possibly of similar strength to $Au(SCN)_4^-$. This was investigated by examining the extraction of 10 μg Au/ml as $AuCl_4^-$ and $Au(SCN)_4^-$ into amyl methyl ketone in the absence and presence of 50 mg THA-1. In the absence of THA-1, 90% of the $AuCl_4^-$ and 85% of the $Au(SCN)_4^-$ were extracted in two minutes. With THA-1 present the extraction of $AuCl_4^-$ decreased to 30% whereas that of $Au(SCN)_4^-$ remained at 85%. The lower extraction of $AuCl_4^-$ could be due to the displacement of Cl^- by humic acids to yield stronger non-extractable complexes with gold. Alternatively since the oxidation potential of the humic acids is less positive than

that of $AuCl_4^-$, reduction to metallic gold would also cause a decrease in the extraction. In the case of $Au(SCN)_4^-$, the fact that humic acids have no effect on the extraction is an indication that the stabilities of the thiocyanate complex and those with humic acids are of the same order of magnitude.

8.5 X-ray diffraction investigation of the association of gold with humic acids

As was seen in Chapter 7 (section 7.1) X-ray diffraction offers a means of investigating the fate of chemical compounds and minerals when they are associated with solutions of humic acids.

In an association of gold with humic acids the metal may exist as a dispersed colloidal phase or as some form of complex. Provided that the association contains sufficient gold to be detected by X-ray diffraction it should be possible to distinguish between these two possibilities. It was found that when 1 mg of colloidally dispersed gold was dried in the presence of 100 mg of humic acids, the Au(111) planes yielded a sharp diffraction peak. The results of the solution experiment however, indicate that the time required to produce such high contents of gold in humic acids, under conditions approaching those in nature would be extremely long.

A concentred association of gold with humic acids was produced by mixing 2 mg Au as $HAuCl_4$ with 20 ml of 1% THA-1. The solution was adjusted to pH = 5 with NH_4OH and 10 mg of $KMnO_4$ were added to ensure the dissolution of the gold. After shaking for 24 hours the humic acids were precipitated by the addition of $Al_2(SO_4)_3$, separated by centrifuging and dried. The gold content of the residual solution was less than 0.1 mg/l whereas analysis of the dried humic acids revealed a gold content of 0.9%.

The gold humates and the colloidal dispersion of 1 mg Au in 100 mg THA-1 were examined by X-ray diffraction. The resulting

diffractograms are illustrated in Figure 33. It is apparent from the strength of the diffraction by the Au (111) planes that the metal is present only in the physical mixture with THA-1. The reaction of gold with the solution of humic acids produced an amorphous complex of the metal.

8.6 Summary and discussion

The possible means of gold transport in the weathering cycle include ionic, colloidal and organic complexation. The low content of gold in river water, stated by Fischer (1966) to be 0.002 µg/l, prevents direct assessment of these possibilities. Ionic and colloidal transport require that gold enters the hydrosphere largely as $AuCl_4^-$. Krauskopf (1967) has shown that $AuCl_4^-$ can be produced during weathering of a gold bearing ore body. The conditions necessary for this to occur are that both H^+ and Cl^- are present, with one of these in relatively high concentration and in addition on oxidising agent, such as MnO_2, must also be present. As Krauskopf (1967) points out, such conditions occur rarely and result only locally in appreciable transport of gold.

Ong and Swanson (1969) have calculated the theoretical concentration of gold in river water from mean composition values (Livingstone, 1963) and equilibrium constant data for the various possible ionic gold species (Martell and Sillen, 1964). The maximum value obtained of $10^{-10.5}$ M (0.006 µg/l) is compatible with the concentration given by Fischer (1966). At pH 4 the dominant species was found to be $AuCl_2^-$ whereas at pH 9 it was AuO_2^-. This presents a problem at the lower pH since, as Baes and Mesmer (1976) indicate, Au^{+3} produces more stable species than Au^{+1} and, in the presence of the latter valence state, disproportionation reactions of the type :

$$3 AuX_2^- \rightleftharpoons AuX_4^- + 2Au^0 + 2X^-$$ will occur. If the stable species is
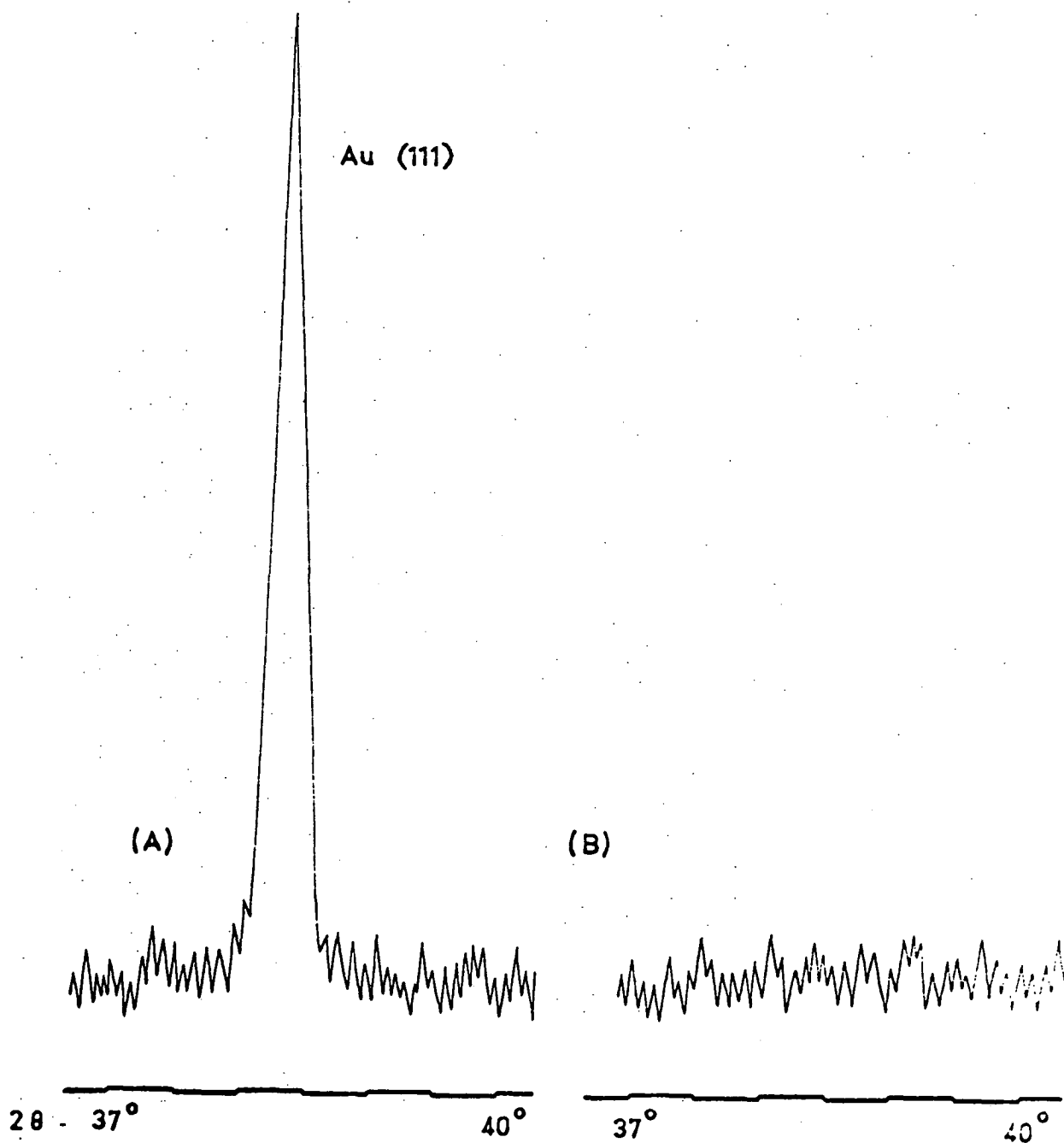
Figure 33. *X-ray diffraction results for (A) 1 mg colloidal Au in physical admixture with 100 mg THA-1 and (B) 1 mg Au as HAuCl₄ reacted 24 hours with 10 ml 1% THA-1 in presence of KMnO₄.*

$AuCl_4^-$, then the theoretically possible concentration of 10^{-17}M

as calculated by Ong and Swanson (1969) indicates that the observed

concentration cannot be explained in terms of this ion. Baes and

Mesmer (1976) have also noted the existence of the neutral complexes

$AuCl_3$, $Au(OH)_3$, $Au(OH)Cl_2$ and $Au(OH)_2Cl$ which, with solubilities of

the order of $10^{-5.5}$ M (0.6 ppm), would more than adequately solve the

concentration problem. However since $AuCl_3$ is stable only at pH >2

and also, for the reaction: $Au(OH)_3 + 3H^+ + 3e^- \rightleftharpoons Au^0 + 3H_2O$,

$\Delta G = -5.8 \times 10^5$ joule/mole (-140 k cal/mole), it is unlikely that

these species would occur under natural conditions. The formation

of the very stable $Au(CN)_2^-$ ion by the action of cyanoglycosides could

explain the gold uptake by plants but, as Lakin *et al.* (1974) comment

$Au(CN)_2^-$ would have limited mobility due to the rapid hydrolysis and

enzymic destruction of the CN^- ion in nature. Thus the mobility of

gold in the weathering cycle does not appear to be adequately explained

in terms of inorganic complexes of gold.

There is no doubt that the molecular weight range of humic

substances, estimated by Dubach and Mehta (1963) to be in the range

of 2000 to 300 000, demands that a large proportion of such molecules

are of colloidal size. Colloidal phenomena have been observed by

Ong and Swanson (1969) in experiments with gold and humic acids. These

investigators found that $AuCl_4^-$ was reduced to colloidal gold in the

presence of humic acids which were also found to act as a protective

colloid for the gold sol so formed. As a result of such observations

a colloidal model of gold mobilisation in the weathering cycle was

proposed. Although the reducing groups of humic acids are capable

of producing colloidal gold from $AuCl_4^-$ the problem of concentration

of the former ion remains. Also, given sufficient residence time in

an environment with an excess of humic acids, it is likely that the

complexing groups of these materials will react with colloidal gold to produce complexes of the metal.

The results of experiments reported above clearly indicate the complexation of gold by humic acids. The gold solubility in the presence of 500 mg/l humic acids, which was up to 300 µg/l is far in excess of that found in river water (0.002 µg/l). An organic complexation model could thus readily explain the observed gold solubility in the hydrosphere. Although analytical restrictions made it necessary to carry out experimental work at higher concentrations than those in nature, the results are believed to be applicable to the mobilisation of gold. In the experiments the concentration of humic acids was kept well in excess of gold, as is the case in the natural environment. Whereas the content of humic substances in river water is highly variable, a value of only 5 µg/ml (ppm) would be in excess of gold by the order of 10^6. From a more general point of view, Reuter and Perdue (1977) have shown that complexation of trace metals in river waters by humic substances can be significant even in the presence of high excesses of major cations.

The concept that gold cannot be complexed by humic acids derives from the fact that complexation involves oxidation, and that humic acids have been generally considered reducing agents. Although reducing conditions occur in areas of peat formation, such conditions are not necessarily due to the presence of humic acids nor do they apply universally to interfaces between soil and rock. The Eh values of the 500 mg/l preparations of humic acids, which are of the order of +300 mV, indicate that these are not strongly reducing in character. Waters such as these, which contain atmospheric oxygen, would be relatively common in soil profiles where free drainages exists. Szilagyi (1971) made a comprehensive study of the redox characteristics of

suspensions of peat humic acids in H_2O and derived a value for E_0 of +0.7 V. Shcherbina (1956) has noted that the redox potential of complexes of gold decreases with their increasing stability. Thus for reactions of the type: $AuX_4^- + 3e \rightleftharpoons Au^0 + 4X^-$ where X is respectively Cl^-, Br^- and SCN^- the E_0 values are +1.00 V. +0.86 V and +0.66 V. If the stability of the complexes of humic acids with gold is near that of $Au(SCN)_4^-$, as suggested by Shcherbina (1956) and supported by the solvent extraction results, it is possible that oxidation of gold can occur under natural conditions.

Draeger and Lauer (1967) have noted that almost 70% of the earth's land surface is covered by forest or grassland. The sulphide deposits carrying gold, from which $AuCl_4^-$ may be readily generated, occupy an insignificant proportion of this surface. It therefore seems plausible that a substantial amount of gold, which has its origin as a trace element in the lithosphere, is mobilised by some process other than the formation of $AuCl_4^-$. Humic acids, originating through microbial action in the products of degeneration of the extensive vegetation cover, appears well suited to such a role. Since they are present in soil water from the time of formation of the interface between soil and rock, they could generate complexes of humic acids with gold by reaction with traces of the metal. Such complexes of gold are not subject to the problems of stability and solubility, to the same degree as ionic or colloidal gold, and they could migrate readily in the hydrosphere.

CHAPTER 9

GENERAL SUMMARY AND CONCLUSIONS.

The effects of humic acids on non-silicate minerals and the
characteristics of the metal humates, which were investigated by
a number of procedures, have been discussed in this thesis. The
humic acids studied were extracted from north-western and western
Tasmanian soils of podzolic affinities. A large proportion of the
organic matter of these soils is humic acids which are relatively
mobile as is general for occurrences of these substances in podzols
(Kononova, 1966). The chemical data that were acquired with the
available equipment reveal that the Tasmanian samples, although from
soils of podzolic type, have a range in composition and optical
properties different from the podzol (*sensu strictu*) of the Northern
Hemisphere. Possibly some future detailed chemical study may provide
interesting data on the relationships between Tasmanian indigenous
flora and the humic acids which result from their decay.

There can be no doubt about the aggressive capabilities of the
humic acids in the weathering cycle. Since the writer's interests
are in the field of applied geochemistry the majority of studies have
been concerned with the minerals of economic deposits. Most sulphide
minerals are more rapidly degraded than silicates by humic acids.
Iron and manganese oxides together with numerous secondary minerals
produced during the oxidation of an ore body are particularly vulnerable.
These features of the activity of humic acids may explain the poor
development of gossans in Tasmania during the current erosional cycle.
In a number of localities, sulphides may be seen to be weathering at
the surface with little evidence of oxides or secondary minerals
being developed. Apparently the rate of solution is sufficiently
rapid for the metals to pass into solution as humates. It is likely

that the few substantial developments of gossans in western Tasmania were produced during a past erosional cycle. Since the glaciation of the Pleistocene, Tasmania has had a cool, wet temperate climate and it is under these conditions that humic substances are probably most active. Their activity is likely to present a serious problem in geochemical prospecting. In circumstances where the chemical activity exceeds the physical removal of weathered products and consequential exposure of new materials, secondary dispersion patterns may be weakened or entirely obliterated by removal of the trace metals from the profile as mobile humates.

Over twenty years ago Schatz *et al.* (1954) suggested that complexation was an active weathering process and that possibly humic substances were complexing agents. Little notice was subsequently taken of this proposal and in fact, to the contrary, it was suggested that since humic substances were reducing agents they could not complex metals because this process involves oxidation (*e.g.* Ong and Swanson, 1969). The study of solubility of pure metals in humic acids reveals that these substances must be far more active as complexing agents than as reductants. Szilagyi (1971) determined an E_0 value for peat humic acids of +0.7V which is more positive than has been generally accepted. Ong and Swanson (1969), for example suggested a value of less than +0.447V. The polarographic studies of Fe^{+3} and U^{+6} are consistent with the higher value which was assigned by Szilagyi (1971). The study of gold reported in this thesis demonstrates that this metal may be complexed by humic acids. The gold solubility shows that in the presence of humic acids the normal reduction potential for $Au^{+3} + 3e \rightleftharpoons Au^0$ of +1.42V must be decreased to a value of less than +0.7V. Since the presence of thiocyanate, for example, causes a decrease to +0.66V

there is no reason to expect that naturally occurring complexing agents cannot achieve the same result.

In view of the rapid dissolution of iron in humic acids and the fact that silicates are attacked, it is pertinent to consider the fate of concrete structures. From a study of Portland cement it was found that this material released 5.3 mg Ca to a 1 g/l solution of THA-1 during a period of 24 hours. This suggests than in an environment where humic acids are active it would be essential to make use of protective drainage, to ensure a reasonable life expectancy for concrete piping or foundations.

Several papers (Ong and Bisque, 1968; Ong and Swanson, 1969; Ong et al., 1970) have stressed the importance of colloidal properties of humic acids in the weathering cycle. Experimental studies, such as those of Ong and Bisque (1968), which show that interactions between humic acids and cations are compatible with the Schulze-Hardy rule and DLVO theory are generally carried out at far higher electrolyte concentrations than are found in nature. The observed colloidal phenomena are the result of the rapid neutralisation of negative charges on the humic acids by the presence of a high concentration of cations. This mechanism of interaction is restricted to estuarine and mineral spring environments or to regions where human pollution provides an excessively high supply of cations. The writer takes the view that whilst aggregates of molecules of humic acids range into colloidal dimensions, the major activity of these substances is by means of complexation.

In nature, an aqueous solvent carrying a relatively high concentration of humic substances (possibly up to 500 mg/l) which is generated in the soil layer, percolates along the interface between soil and rock. Hence the reactions which occur are not the result of

a colloidal response to the presence of a high concentration of cations, but rather one of a solvent acting on solid mineral surfaces. This results in the gradual removal of cations from the lattices of minerals by a complexation mechanism. Some of the complexes are dispersed in the hydrosphere at concentrations well below those likely to give rise to colloidal instability whilst others remain temporarily in the soil. The study of leaching by humic acids shows that in wet temperate climates the continual generation of solvents in the soil will ensure eventual migration of most humates. Only aluminium humate appears to be resistant to transport and this is in keeping with the suggestion by Harden and Bateson (1963), Grubb (1970), Petersen (1971) and others that humic substances are active in removing components other than aluminium, in bauxite formation.

The evidence from potentiometric titrations, polarography, electrophoresis and infra-red spectra independently support the view the complexation is an important mechanism in the interaction between humic substances and cations. This does not exclude such other phenomena as salt formation and adsorption which also contribute to the association. Complexation reactions are often of first order and as has been shown for several lead minerals the interactions of humic acids followed first order kinetics. This suggests that extrapolation from the laboratory to nature can be undertaken with reasonable certainty.

The ultimate destination of much of the humic substances generated on the land must be the seas. The average total discharge from the major rivers of western Tasmania, of which a typical example is shown in Plate I, is of the order of 3.0×10^{10} m^3 annually from an aggregate catchment of about 20 000 km^2. Even with an estimate for the average content of humic substances as low as 5 mg/l the resulting quantity delivered to the sea each year is 150 000 tonnes.

Given that the formation of an ore body may be the result of several

Plate I.   Franklin River - a typical example of the
          drainage waters of Western Tasmania.

stages of concentration, it is possible that the ability of humic
acids to transport metals may be an important early event. In
restricted areas, the excessive weathering of existing ore bodies
and dispersed mineralisation in the presence of humic substances
may result in higher than average metal concentrations being
developed in swamps, estuaries and near shore marine environments.
Whilst these are unlikely to represent economic sources of metals
at this stage they are undoubtedly associations from which subsequent
processes could produce ore bodies. Thus a cycle may exist in which
the humic substances prevent the wide dispersion of metals which
would be likely to occur if transport was largely an ionic phenomenon.

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APPENDIX 1

ANALYTICAL DATA FOR THE REACTION OF MINERALS
AND METALS WITH DISTILLED H_2O IN EQUILIBRIUM
WITH ATMOSPHERIC CO_2, HUMIC ACIDS,
SIMPLE ORGANIC COMPOUNDS AND DISTILLED H_2O
IN THE PRESENCE OF A CO_2 ENRICHED ATMOSPHERE

Table 1. *REACTION OF MINERALS WITH DISTILLED H_2O IN EQUILIBRIUM WITH ATMOSPHERIC CO_2. (H_2O/ATMOS. CO_2)*

Mineral		Element determined	μg/ml metal in solution after 24 hours		
			Run 1	Run 2	Average
Galena	PbS	Pb	1.2	0.9	1.1
Bornite	Cu_5FeS_4	Cu	1.8	2.2	2.0
Sphalerite	ZnS	Zn	1.3	1.8	1.6
Pyrite	FeS	Fe	0.7	1.0	0.9
Loellingite	FeAsS	Fe	0.9	1.3	1.1
Bismuthinite	Bi_2S_3	Bi	0.8	0.5	0.7
Stibnite	Sb_2S_3	Sb	0.2	0.3	0.3
Hematite	Fe_2O_3	Fe	1.2	1.0	1.1
Magnetite	Fe_3O_4	Fe	1.8	2.2	2.0
Pyrolusite	MnO_2	Mn	3.0	3.6	3.3
Azurite	$Cu_3(OH)_2(CO_3)_2$	Cu	4.5	3.8	4.2
Anglesite	$PbSO_4$	Pb	3.2	2.7	3.0
Calcite	$CaCO_3$	Ca	12.4	14.0	13.0
Dolomite	$(Ca,Mg)CO_3$	Ca	4.5	5.2	4.9
		Mg	5.4	6.1	2.7
Magnesite	$MgCO_3$	Mg	3.8	4.7	4.3

Table 2. REACTION OF MINERALS WITH 500 mg/l SOLUTION OF THA-1 IN H_2O/ATMOS. CO_2.

Mineral		Element determined	μg/ml metal in solution after 24 hours		
			Run 1	Run 2	Average
Galena	PbS	Pb	56.6	48.1	52.4
Bornite	Cu_5FeS_4	Cu	23.7	24.7	24.2
Sphalerite	ZnS	Zn	2.4	2.7	2.6
Pyrite	FeS_2	Fe	5.0	4.3	4.7
Loellingite	$FeAs_2$	Fe	103.4	99.4	101.4
Bismuthinite	Bi_2S_3	Bi	44.8	37.3	41.1
Stibnite	Sb_2S_3	Sb	3.1	2.4	2.8
Hematite	Fe_2O_3	Fe	11.2	12.0	11.6
Magnetite	Fe_3O_4	Fe	9.4	11.9	10.7
Pyrolusite	MnO_2	Mn	27.3	31.5	29.4
Azurite	$Cu_3(OH)_2(CO_3)_2$	Cu	458.0	424.0*	441.0
Anglesite	$PbSO_4$	Pb	1120.0	1104.0*	1112.0
Calcite	$CaCO_3$	Ca	319.0	376.0*	348.0
Dolomite	$(Ca,Mg)CO_3$	Ca	157.0	143.0*	150.0
		Mg	116.0	110.0*	113.0
Magnesite	$MgCO_3$	Mg	20.0	22.5	21.3

*Estimated from a 3 hour run

Table 3. REACTION OF MINERALS WITH 500 mg/l SOLUTION OF THA-2 IN H_2O/ATMOS. CO_2.

Mineral		Element determined	μg/ml metal in solution after 24 hours		
			Run 1	Run 2	Average
Galena	PbS	Pb	33.8	26.4	30.1
Bornite	Cu_5FeS_4	Cu	16.7	22.5	19.6
Sphalerite	ZnS	Zn	2.0	2.2	2.1
Pyrite	FeS_2	Fe	12.7	11.1	11.9
Loellingite	$FeAs_2$	Fe	56.0	65.0	60.5
Bismuthinite	Bi_2S_3	Bi	46.0	55.2	50.6
Stibnite	Sb_2S_3	Sb	8.8	10.4	9.6
Hematite	Fe_2O_3	Fe	3.3	4.3	3.8
Magnetite	Fe_3O_4	Fe	24.5	17.4	21.0
Pyrolusite	MnO_2	Mn	17.7	13.3	15.5
Azurite	$Cu_3(OH)_2(CO_3)_2$	Cu	249.0	234.0*	242.0
Anglesite	$PbSO_4$	Pb	478.0	534.0*	506.0
Calcite	$CaCO_3$	Ca	221.0	234.0*	228.0
Dolomite	$(Ca,Mg)CO_3$	Ca	100.0	100.0*	100.0
		Mg	76.0	74.0*	75.0
Magnesite	$MgCO_3$	Mg	17.7	19.5	18.6

*Estimated from a 3 hour run

Table 4. REACTION OF MINERALS WITH 500 mg/l SOLUTION OF THA-3
IN H_2O/ATMOS. CO_2.

Mineral		Element determined	µg/ml metal in solution after 24 hours		
			Run 1	Run 2	Average
Galena	PbS	Pb	8.1	7.5	7.8
Bornite	Cu_5FeS_4	Cu	19.2	23.6	21.4
Sphalerite	ZnS	Zn	2.2	2.4	2.3
Pyrite	FeS_2	Fe	2.5	2.3	2.4
Loellingite	$FeAs_2$	Fe	27.8	23.4	25.6
Bismuthinite	Bi_2S_3	Bi	24.4	20.6	22.5
Stibnite	Sb_2S_3	Sb	1.5	1.2	1.4
Hematite	Fe_2O_3	Fe	1.4	1.8	1.6
Magnetite	Fe_3O_4	Fe	2.8	2.6	2.7
Pyrolusite	MnO_2	Mn	12.5	10.2	11.4
Azurite	$Cu_3(OH)_2(CO_3)_2$	Cu	195.0	215.0*	205.0
Anglesite	$PbSO_4$	Pb	1136.0	1088.0*	1112.0
Calcite	$CaCO_3$	Ca	297.0	222.0*	215.0
Dolomite	$(Ca,Mg)CO_3$	Ca	77.0	82.0*	80.0
		Mg	46.0	50.0*	48.0
Magnesite	$MgCO_3$	Mg	8.4	8.8	8.6

*Estimated from a 3 hour run

Table 5.   REACTION OF MINERALS WITH 500 mg/l SOLUTION OF THA-4
           IN H_2O/ATMOS. CO_2.

Mineral		Element determined	µg/ml metal in solution after 24 hours		
			Run 1	Run 2	Average
Galena	PbS	Pb	26.5	24.4	25.5
Bornite	Cu_5FeS_4	Cu	23.5	27.3	25.4
Sphalerite	ZnS	Zn	1.7	2.1	1.9
Pyrite	FeS_2	Fe	2.0	1.7	1.9
Loellingite	$FeAs_2$	Fe	25.5	22.5	24.0
Bismuthinite	Bi_2S_3	Bi	28.8	42.3	40.6
Stibnite	Sb_2S_3	Sb	4.2	3.5	3.9
Hematite	Fe_2O_3	Fe	1.9	1.7	1.8
Magnetite	Fe_3O_4	Fe	7.0	6.4	6.7
Pyrolusite	MnO_2	Mn	23.8	25.9	24.9
Azurite	$Cu_3(OH)_2(CO_3)_2$	Cu	295.0	289.0*	292.0
Anglesite	$PbSO_4$	Pb	610.0	570.0*	590.0
Calcite	$CaCO_3$	Ca	256.0	243.0*	250.0
Dolomite	$(Ca,Mg)CO_3$	Ca	114.0	110.0*	112.0
		Mg	103.0	94.0*	99.0
Magnesite	$MgCO_3$	Mg	17.3	18.2	17.8

*Estimated from a 3 hour run

Table 6. REACTION OF MINERALS WITH 500 mg/l SOLUTION OF THA-5 IN H_2O/ATMOS. CO_2.

Mineral		Element determined	μg/ml metal in solution after 24 hours		
			Run 1	Run 2	Average
Galena	PbS	Pb	20.0	18.2	19.1
Bornite	Cu_5FeS_4	Cu	22.9	25.1	24.0
Sphalerite	ZnS	Zn	1.7	2.1	1.9
Pyrite	FeS_2	Fe	5.9	8.4	7.2
Loellingite	$FeAs_2$	Fe	43.4	40.4	41.9
Bismuthinite	Bi_2S_3	Bi	37.0	40.9	39.0
Stibnite	Sb_2S_3	Sb	0.8	0.6	0.7
Hematite	Fe_2O_3	Fe	5.7	7.7	6.7
Magnetite	Fe_3O_4	Fe	6.2	8.6	7.4
Pyrolusite	MnO_2	Mn	12.3	10.8	11.6
Azurite	$Cu_3(OH)_2(CO_3)_2$	Cu	166.0	157.0*	162.0
Anglesite	$PbSO_4$	Pb	332.0	334.0*	333.0
Calcite	$CaCO_3$	Ca	199.0	208.0*	204.0
Dolomite	$(Ca,Mg)CO_3$	Ca	70.0	66.0*	68.0
		Mg	63.0	57.0*	60.0
Magnesite	$MgCO_3$	Mg	11.4	11.0	11.2

*Estimated from a 3 hour run

Table 7. REACTION OF MINERALS WITH 500 mg/l SOLUTION OF SALICYLIC ACID IN H_2O/ATMOS. CO_2.

Mineral		Element determined	$\mu g/ml$ metal in solution after 24 hours		
			Run 1	Run 2	Average
Galena	PbS	Pb	13.8	15.3	14.6
Bornite	Cu_5FeS_4	Cu	30.6	28.4	29.5
Sphalerite	ZnS	Zn	1.5	1.7	1.6
Pyrite	FeS_2	Fe	1.0	1.2	1.1
Loellingite	$FeAs_2$	Fe	70.4	67.6	69.0
Bismuthinite	Bi_2S_3	Bi	2.7	2.2	2.5
Stibnite	Sb_2S_3	Sb	0.1	0.1	0.1
Hematite	Fe_2O_3	Fe	1.4	1.6	1.5
Magnetite	Fe_3O_4	Fe	9.4	8.8	9.1
Pyrolusite	MnO_2	Mn	58.0	62.6	60.3
Azurite	$Cu_3(OH)_2(CO_3)_2$	Cu	608.0	544.0*	576.0
Anglesite	$PbSO_4$	Pb	280.0	263.0*	272.0
Calcite	$CaCO_3$	Ca	496.0	474.0*	485.0
Dolomite	$(Ca,Mg)CO_3$	Ca Mg	212.0	202.0*	207.0
Magnesite	$MgCO_3$	Mg	20.6	18.8	22.3

*Estimated from a 3 hour run

Table 8. REACTION OF MINERALS WITH 500 mg/l SOLUTION OF CITRIC ACID IN H_2O/ATMOS. CO_2.

Mineral		Element determined	µg/ml metal in solution after 24 hours		
			Run 1	Run 2	Average
Galena	PbS	Pb	17.3	19.2	18.3
Bornite	Cu_5FeS_4	Cu	56.1	64.6	60.4
Sphalerite	ZnS	Zn	1.2	1.6	1.4
Pyrite	FeS_2	Fe	1.7	1.3	1.5
Loellingite	$FeAs_2$	Fe	60.4	65.2	62.8
Bismuthinite	Bi_2S_3	Bi	26.9	25.0	26.0
Stibnite	Sb_2S_3	Sb	0.2	0.3	0.3
Hematite	Fe_2O_3	Fe	1.7	1.5	1.6
Magnetite	Fe_3O_4	Fe	37.0	35.3	36.2
Pyrolusite	MnO_2	Mn	50.6	48.0	49.3
Azurite	$Cu_3(OH)_2(CO_3)_2$	Cu	1498.0	1539.0*	1518.0
Anglesite	$PbSO_4$	Pb	467.0	486.0*	477.0
Calcite	$CaCO_3$	Ca	995.0	960.0*	978.0
Dolomite	$(Ca,Mg)CO_3$	Ca	420.0	411.0*	416.0
		Mg	355.0	325.0*	340.0
Magnesite	$MgCO_3$	Mg	47.2	44.6	45.9

*Estimated from a 3 hour run

Table 9. *REACTION OF MINERALS WITH 500 mg/l SOLUTION OF GLYCINE IN H_2O/ATMOS. CO_2.*

Mineral		Element determined	µg/ml metal in solution after 24 hours		
			Run 1	Run 2	Average
Galena	PbS	Pb	1.5	1.9	1.7
Bornite	Cu_5FeS_4	Cu	75.8	80.2	78.0
Sphalerite	ZnS	Zn	1.5	1.2	1.4
Pyrite	FeS_2	Fe	0.8	1.0	0.9
Loellingite	$FeAs_2$	Fe	1.4	1.2	1.3
Bismuthinite	Bi_2S_3	Bi	22.8	20.9	21.9
Stibnite	Sb_2S_3	Sb	0.5	0.8	0.7
Hematite	Fe_2O_3	Fe	0.9	1.3	1.1
Magnetite	Fe_3O_4	Fe	2.1	1.8	2.0
Pyrolusite	MnO_2	Mn	6.5	8.4	7.5
Azurite	$Cu_3(OH)_2(CO_3)_2$	Cu	794.9	786.0*	795.0
Anglesite	$PbSO_4$	Pb	187.0	173.0*	180.0
Calcite	$CaCO_3$	Ca	80.0	86.0*	83.0
Dolomite	$(Ca,Mg)CO_3$	Ca	18.0	14.0*	16.0
		Mg	22.0	16.0*	19.0
Magnesite	$MgCO_3$	Mg	7.7	6.2	7.0

*Estimated from a 3 hour run

Table 10. REACTION OF MINERALS WITH 500 mg/l SOLUTION OF ALANINE IN H_2O/ATMOS. CO_2.

Mineral		Element determined	μg/ml metal in solution after 24 hours		
			Run 1	Run 2	Average
Galena	PbS	Pb	2.4	1.8	2.1
Bornite	Cu_5FeS_4	Cu	7.0	7.4	7.2
Sphalerite	ZnS	Zn	1.6	1.2	1.4
Pyrite	FeS_2	Fe	1.1	0.8	1.0
Loellingite	$FeAs_2$	Fe	1.4	1.7	1.6
Bismuthinite	Bi_2S_3	Bi	14.8	12.6	13.7
Stibnite	Sb_2S_3	Sb	0.4	0.2	0.3
Hematite	Fe_2O_3	Fe	1.4	1.6	1.5
Magnetite	Fe_3O_4	Fe	2.3	1.9	2.1
Pyrolusite	MnO_2	Mn	3.4	3.8	3.6
Azurite	$Cu_3(OH)_2(CO_3)_2$	Cu	132.0	138.0*	135.0
Anglesite	$PbSO_4$	Pb	190.0	190.0*	190.0
Calcite	$CaCO_3$	Ca	54.0	58.0*	56.0
Dolomite	$(Ca,Mg)CO_3$	Ca	14.0	14.0*	14.0
		Mg	19.0	17.0*	18.0
Magnesite	$MgCO_3$	Mg	5.2	5.9	5.6

*Estimated from a 3 hour run

Table 11. REACTION OF MINERALS WITH 500 m/gl SOLUTION OF CATECHIN in H_2O/ATMOS. CO_2.

Mineral		Element determined	$\mu g/ml$ metal in solution after 24 hours		
			Run 1	Run 2	Average
Galena	PbS	Pb	5.6	4.8	5.2
Bornite	Cu_5FeS_4	Cu	9.4	10.1	9.8
Sphalerite	ZnS	Zn	1.4	1.7	1.6
Pyrite	FeS_2	Fe	1.2	0.8	1.0
Loellingite	$FeAs_2$	Fe	9.4	8.6	9.0
Bismuthinite	Bi_2S_3	Bi	35.0	37.4	36.2
Stibnite	Sb_2S_3	Sb	1.0	0.8	0.9
Hematite	Fe_2O_3	Fe	1.6	1.2	1.4
Magnetite	Fe_3O_4	Fe	3.8	3.2	3.5
Pyrolusite	MnO_2	Mn	7.8	8.6	8.2
Azurite	$Cu_3(OH)_2(CO_3)_2$	Cu	188.0	192.0*	190.0
Anglesite	$PbSO_4$	Pb	244.0	218.0*	231.0
Calcite	$CaCO_3$	Ca	116.0	102.0*	109.0
Dolomite	$(Ca,Mg)CO_3$	Ca	45.0	38.0*	42.0
		Mg	51.0	43.0*	47.0
Magnesite	$MgCO_3$	Mg	7.8	8.2	8.0

*Estimated from a 3 hour run

Table 12. REACTION OF MINERALS WITH 500 mg/l SOLUTION OF FRUCTOSE IN H_2O/ATMOS. CO_2.

Mineral		Element determined	µg/ml metal in solution after 24 hours		
			Run 1	Run 2	Average
Galena	PbS	Pb	1.8	1.4	1.6
Bornite	Cu_5FeS_4	Cu	2.6	1.9	2.3
Sphalerite	ZnS	Zn	1.6	1.4	1.5
Pyrite	FeS_2	Fe	0.6	0.9	0.8
Loellingite	$FeAs_2$	Fe	1.3	2.1	1.7
Bismuthinite	Bi_2S_3	Bi	8.9	7.6	8.3
Stibnite	Sb_2S_3	Sb	0.3	0.4	0.4
Hematite	Fe_2O_3	Fe	1.0	1.3	1.2
Magnetite	Fe_3O_4	Fe	2.4	2.1	2.3
Pyrolusite	MnO_2	Mn	4.3	6.2	5.3
Azurite	$Cu_3(OH)_2(CO_3)_2$	Cu	5.0	6.0*	5.0
Anglesite	$PbSO_4$	Pb	148.0	138.0*	143.0
Calcite	$CaCO_3$	Ca	52.0	58.0*	55.0
Dolomite	$(Ca,Mg)CO_3$	Ca	10.0	12.0*	11.0
		Mg	17.0	19.0*	18.0
Magnesite	$MgCO_3$	Mg	4.6	4.2	4.4

*Estimated from a 3 hour run

Table 13. REACTION OF MINERALS WITH H_2O IN THE PRESENCE OF CO_2 ENRICHED AIR. (28 ml $CO_2 \backsimeq 0.025$ g HUMIC ACID).

Mineral		Element determined	µg/ml metal in solution after 24 hours		
			Run 1	Run 2	Average
Galena	PbS	Pb	4.2	5.1	4.7
Pyrolusite	MnO_2	Mn	4.4	3.9	4.2
Calcite	$CaCO_3$	Ca	51.5	54.3	52.9
Dolomite	$(Ca,Mg)CO_3$	Ca	8.8	9.2	9.0
		Mg	6.4	6.7	6.6
Magnesite	$MgCO_3$	Mg	5.2	5.8	5.5

Table 14. REACTION OF METALS WITH 500 mg/l SOLUTIONS OF THA-1 AND THA-4 AND H_2O/ATMOS. CO_2.

Solvent	Metal	μg/ml metal in solution after 15 minutes extraction by humic acids		
		Run 1	Run 2	Average
THA-1	Iron	38.7	48.8	43.8
	Copper	32.0	36.6	34.3
	Lead*	106	67	87
	Zinc	70	74	72
	Bismuth	12.4	16.5	14.5
	Antimony	27.5	31.5	29.5
THA-4	Iron	25.2	28.2	26.7
	Copper	23.7	27.5	25.6
	Lead*	74	56	65
	Zinc	45	52	48
	Bismuth	5.0	5.1	5.0
	Antimony	26.0	28.1	27.1
H_2O/Atmos. CO_2	Iron	1.4	1.2	1.3
	Copper	0.1	0.1	0.1
	Lead*	24.2	21.3	22.8
	Zinc	0.3	0.3	0.3
	Bismuth	0.1	0.1	0.1
	Antimony	27.8	28.5	28.2

*Metal extracted in 5 minutes.

APPENDIX 2

pH DATA FOR HUMIC ACID INTERACTION

WITH CATIONS

Table 15. *DECREASE IN pH ACCOMPANYING ADDITION OF 200 μ eq CATIONS TO 50 ml 1 g/l SOLUTIONS OF HUMIC ACIDS INITIALLY AT pH = 4*

Humic acid	Run No.	pH value after addition of								
		Ag^{+1}	Ca^{+2}	Co^{+2}	Cu^{+2}	Mg^{+2}	Mn^{+2}	Ni^{+2}	Pb^{+2}	Zn^{+2}
THA-1	1	3.50	3.36	3.25	2.97	3.45	3.30	3.21	2.98	3.33
	2	3.58	3.28	3.33	3.13	3.53	3.36	3.31	2.94	3.39
	Av.	3.54	3.32	3.29	3.05	3.49	3.33	3.26	2.96	3.36
THA-2	1	3.59	3.49	3.52	3.32	3.48	3.49	3.52	3.03	3.46
	2	3.55	3.55	3.46	3.26	3.60	3.47	3.42	3.11	3.54
	Av.	3.57	3.52	3.49	3.29	3.54	3.48	3.47	3.07	3.50
THA-3	1	3.62	3.38	3.40	3.13	3.55	3.45	3.34	2.94	3.32
	2	3.58	3.46	3.38	3.19	3.53	3.35	3.36	3.02	3.36
	Av.	3.60	3.42	3.39	3.16	3.54	3.40	3.35	2.98	3.34
THA-4	1	3.81	3.68	3.55	3.38	3.73	3.62	3.58	3.27	3.63
	2	3.77	3.64	3.65	3.34	3.81	3.68	3.60	3.25	3.69
	Av.	3.79	3.66	3.60	3.36	3.77	3.65	3.59	3.26	3.66
THA-5	1	3.78	3.64	3.69	3.48	3.77	3.71	3.61	3.45	3.74
	2	3.79	3.76	3.65	3.46	3.87	3.67	3.69	3.39	3.72
	Av.	3.77	3.70	3.67	3.47	3.82	3.69	3.65	3.42	3.73

Table 16. *pH AND FREE CATION DATA AFTER ADDITION OF 200 μ eq CATIONS TO 50 ml OF A 1 g/l THA-1 SOLUTION AND DIALYSIS FOR 2 DAYS*

Cation	pH			Cations not held by THA-1 (μ eq/ml)		
	Run 1	Run 2	Average	Run 1	Run 2	Average
Ag^{+1}	3.26	3.22	3.24	3.58	3.64	3.61
Ca^{+2}	3.09	3.17	3.13	3.32	3.20	3.26
Co^{+2}	3.14	3.18	3.16	3.20	3.30	3.25
Cu^{+2}	2.93	2.93	2.93	2.64	2.60	2.62
Mg^{+2}	3.24	3.20	3.22	3.64	3.68	3.66
Mn^{+2}	3.12	3.16	3.14	3.22	3.28	3.25
Ni^{+2}	3.13	3.11	3.12	3.24	3.32	3.28
Pb^{+2}	2.85	2.84	2.85	2.28	2.26	2.27
Zn^{+2}	3.14	3.10	3.12	3.36	3.42	3.39

Table 17. pH AND FREE CATION DATA AFTER ADDITION OF 200 μ eq CATIONS
TO 50 ml OF A 1 g/l THA-4 SOLUTION AND DIALYSIS FOR 2 DAYS

Cation	pH			Cations not held by THA-1 (μ eq/ml)		
	Run 1	Run 2	Average	Run 1	Run 2	Average
Ag^{+1}	3.09	3.05	3.07	3.76	3.70	3.73
Ca^{+2}	3.00	3.04	3.02	3.68	3.74	3.71
Co^{+2}	3.01	3.01	3.01	3.50	3.60	3.55
Cu^{+2}	2.80	2.82	2.81	2.74	2.76	2.75
Mg^{+2}	3.05	3.05	3.05	3.82	3.76	3.79
Mn^{+2}	3.00	3.02	3.01	3.54	3.42	3.48
Ni^{+2}	2.98	3.00	2.99	3.50	3.54	3.52
Pb^{+2}	2.78	2.77	2.78	2.60	2.64	2.62
Zn^{+2}	2.99	2.99	2.99	3.60	3.64	3.62

APPENDIX 3

POTENTIOMETRIC TITRATION DATA

Table 18.   POTENTIOMETRIC TITRATION OF 50 ml OF 4 g/l SOLUTION
            OF THA-1 AND THA-4 (0.2 g) BY 0.1 meq/ml NaOH.

| meq NaOH | pH values | |
added	THA-1	THA-4
0	2.97	2.85
0.1	3.22	3.04
0.2	3.53	3.30
0.3	3.93	3.56
0.4	4.46	3.84
0.5	4.98	4.23
0.6	5.55	4.61
0.7	6.26	5.02
0.8	7.22	5.51
0.9	8.12	6.08
1.0	8.80	6.84
1.1	9.52	7.87
1.2	10.24	8.77
1.3	10.73	9.53
1.4	11.02	10.15
1.5	11.18	10.59

Table 19. POTENTIOMETRIC TITRATION OF 50 ml OF 10 μ eq/ml VARIOUS
CATIONS WITH 0.1 meq/ml NaOH

meq NaOH added	pH values					
	Ag^{+1}	Co^{+2}	Cu^{+2}	Ni^{+2}	Pb^{+2}	Zn^{+2}
0	3.18	3.04	3.05	2.89	3.03	2.90
0.1	8.99	5.03	4.95	3.09	5.15	3.56
0.2	9.35	8.37	5.03	3.34	5.55	7.55
0.3	10.00	8.50	5.12	3.65	5.98	7.77
0.4	10.69	8.65	5.41	4.02	10.20	7.87
0.5	11.03	9.02	10.36	4.30	10.32	8.03
0.6	11.22	10.53	10.96	5.04	10.89	8.40
0.7	11.33	11.01	11.16	5.78	11.15	9.66
0.8	11.43	11.22	11.30	6.67	11.29	10.67
0.9	11.52	11.35	11.40	7.21	11.40	11.01
1.0	11.58	11.44	11.48	7.63	11.48	11.19
1.1	11.64	11.53	11.55	8.16	11.55	11.32
1.2	11.69	11.60	11.61	8.69	11.61	11.42
1.3	11.73	11.65	11.66	9.39	11.66	11.50
1.4	11.77	11.70	11.70	10.00	11.70	11.56
1.5	11.79	11.75	11.74	10.54	11.74	11.62

Table 20. *POTENTIOMETRIC TITRATION OF 50 ml OF 10 μ eq/ml VARIOUS CATIONS IN THE PRESENCE OF 0.2 g THA-1 WITH 0.1 meq/ml NaOH*

meq NaOH added	pH values					
	Ag^{+1}	Co^{+2}	Cu^{+2}	Ni^{+2}	Pb^{+2}	Zn^{+2}
0	2.88	2.89	2.77	2.89	2.76	2.91
0.1	3.06	3.10	2.91	3.09	2.91	3.09
0.2	3.32	3.36	3.09	3.34	3.09	3.33
0.3	3.64	3.67	3.28	3.65	3.30	3.63
0.4	4.02	4.05	3.51	4.02	3.54	3.95
0.5	4.44	4.47	3.79	4.30	3.89	4.35
0.6	4.96	5.03	4.17	5.04	4.40	4.87
0.7	5.60	5.73	4.74	5.78	5.27	5.53
0.8	6.33	6.62	5.59	6.67	6.24	6.38
0.9	7.31	7.26	6.57	7.21	7.03	6.99
1.0	8.04	7.68	7.14	7.63	7.59	7.38
1.1	8.60	8.09	7.57	8.16	8.28	7.84
1.2	9.30	8.50	8.20	8.69	8.86	8.40
1.3	9.79	9.07	8.95	9.39	9.51	8.87
1.4	10.20	9.88	9.50	10.00	10.08	9.31
1.5	10.57	10.35	10.10	10.54	10.31	9.67

Table 21. POTENTIOMETRIC TITRATION OF 50 ml OF 10 μ eq/ml VARIOUS
CATIONS IN THE PRESENCE OF 0.2 g THA-4 WITH 0.1 meq/ml
NaOH

meq NaOH added	pH values					
	Ag^{+1}	Co^{+2}	Cu^{+2}	Ni^{+2}	Pb^{+2}	Zn^{+2}
0	2.82	2.78	2.72	2.73	2.67	2.76
0.1	2.96	2.90	2.85	2.90	2.80	2.92
0.2	3.18	3.08	3.01	3.11	2.96	3.13
0.3	3.40	3.30	3.17	3.35	3.12	3.36
0.4	3.64	3.55	3.34	3.61	3.32	3.60
0.5	3.96	3.82	3.53	3.86	3.53	4.17
0.6	4.24	4.13	3.74	4.19	3.77	4.52
0.7	4.57	4.49	4.03	4.55	4.07	4.91
0.8	4.89	4.82	4.35	4.98	4.54	5.37
0.9	5.22	5.30	4.81	5.45	5.20	5.97
1.0	6.08	5.81	5.39	6.00	5.97	6.63
1.1	6.91	6.46	6.11	6.74	6.82	7.23
1.2	7.58	7.20	6.83	7.35	7.48	7.84
1.3	8.24	7.64	7.47	8.03	8.12	8.31
1.4	9.09	8.35	8.01	8.65	8.58	8.67
1.5	9.54	9.27	8.64	9.05	9.07	9.06

Table 22. *POTENTIOMETRIC TITRATION OF 50 ml OF 10 μ eq/ml VARIOUS*
CATIONS IN THE PRESENCE OF 0.2 g MnO$_2$ WITH 0.1 μ eq/ml
NaOH

meq NaOH added	pH values					
	Ag^{+1}	Co^{+2}	Cu^{+2}	Ni^{+2}	Pb^{+2}	Zn^{+2}
0	3.22	3.38	3.19	3.55	2.86	3.63
0.1	4.04	4.45	3.71	5.20	3.75	5.50
0.2	5.50	6.03	4.50	7.27	4.80	7.00
0.3	7.63	7.10	5.19	7.87	6.05	7.42
0.4	8.96	7.81	5.56	8.28	7.50	7.79
0.5	9.89	8.22	7.25	8.67	9.67	8.11
0.6	10.54	9.49	9.46	9.60	10.45	8.84
0.7	10.88	10.15	10.49	10.51	10.93	9.67
0.8	11.09	10.66	10.84	10.88	11.13	10.40
0.9	11.23	10.93	11.13	11.11	11.27	10.80
1.0	11.34	11.12	11.27	11.26	11.39	11.07
1.1	11.43	11.25	11.37	11.37	11.48	11.25
1.2	11.50	11.34	11.46	11.46	11.55	11.37
1.3	11.57	11.43	11.54	11.54	11.61	11.46
1.4	11.62	11.50	11.59	11.60	11.67	11.54
1.5	11.67	11.56	11.65	11.65	11.72	11.61

APPENDIX 4

DATA FROM ELUTION STUDIES OF

METAL HUMATES AND ADSORBED CATIONS

Table 23. *ELUTION OF VARIOUS METAL HUMATES PREPARED FROM 25 mg THA-1 WITH 10 ml ALIQUOTS OF DISTILLED H_2O FOLLOWED BY 10 ml ALIQUOTS OF A SOLUTION OF 500 mg/l THA-1*

Type and No. of aliquot		Metals leached from humate (μg/ml)									
		Al^{+3}	Ca^{+2}	Co^{+2}	Cu^{+2}	Fe^{+3}	Mg^{+2}	Mn^{+2}	Ni^{+2}	Pb^{+2}	Zn^{+2}
H_2O	1	1	2.0	2.4	2.2	0.8	1.0	2.2	2.4	0.8	0.7
	2	1	2.0	2.4	2.2	0.8	1.0	2.1	2.4	0.8	0.5
	3	<1	2.0	2.2	0.7	0.8	0.8	2.1	2.3	0.7	0.5
	4	<1	1.8	2.2	0.4	0.7	0.8	2.0	2.3	0.6	0.2
	5	<1	1.6	2.2	0.3	0.5	0.7	1.8	2.2	0.2	0.1
	6	<1	1.6	2.1	0.2	0.5	0.6	1.8	2.3	0.1	0.1
	7	<1	1.4	1.8	0.1	0.3	0.6	1.4	1.5	<0.1	0.1
	8	<1	1.2	2.1	0.1	0.1	0.6	0.8	1.2	<0.1	<0.1
	9	<1	1.2	1.5	0.1	<0.1	0.6	0.8	1.2	<0.1	<0.1
	10	<1	1.2	1.5	0.1	<0.1	0.6	0.5	1.2	<0.1	<0.1
THA-1	1	<1	9.0	9.1	15.9	3.2	3.0	3.8	10.3	60.0	13.1
	2	<1	5.5	7.7	7.8	2.7	2.4	2.7	10.3	52.7	11.4
	3	<1	3.2	6.1	4.3	2.7	1.5	2.7	8.5	28.0	8.5
	4	<1	2.9	4.8	2.8	1.8	1.2	1.6	7.6	19.7	6.5
	5	<1	2.6	4.0	2.5	1.8	1.2	1.6	6.5	15.5	5.6
	6	<1	2.6	3.5	2.0	1.3	1.0	1.6	6.5	15.7	4.6
	7	<1	2.4	3.6	2.1	0.9	1.0	1.4	5.6	12.4	4.5
	8	<1	2.2	3.2	1.8	0.9	1.0	0.5	5.3	11.4	3.7
	9	<1	2.2	2.7	1.4	0.9	0.7	0.5	5.0	10.4	3.5
	10	<1	2.2	2.5	0.9	0.9	0.7	0.5	4.4	9.3	3.5
THA-1 in final H_2O aliquot (μg/ml)		<2	55	50	<2	<2	52	25	45	<2	<2

Table 24. ELUTION OF VARIOUS METAL HUMATES PREPARED FROM 25 mg THA-4
WITH 10 ml ALIQUOTS OF DISTILLED H_2O FOLLOWED BY 10 ml
ALIQUOTS OF A SOLUTION OF 500 mg/l THA-4

Type and No. of aliquot		Metals leached from humate ($\mu g/ml$)									
		Al^{+3}	Ca^{+2}	Co^{+2}	Cu^{+2}	Fe^{+3}	Mg^{+2}	Mn^{+2}	Ni^{+2}	Pb^{+2}	Zn^{+2}
H_2O	1	1	1.6	2.3	0.5	1.6	1.2	3.0	2.2	3.1	0.8
	2	1	1.4	2.1	0.1	1.5	1.2	3.0	2.0	2.4	0.7
	3	1	1.4	2.1	<0.1	1.5	1.0	2.6	1.8	1.0	0.3
	4	1	1.4	2.0	<0.1	1.4	1.1	2.8	1.8	0.6	0.3
	5	<1	1.2	1.8	<0.1	1.6	1.1	2.8	1.8	0.4	0.2
	6	<1	0.8	1.8	<0.1	1.3	0.7	1.6	1.2	0.4	0.2
	7	<1	0.8	1.2	<0.1	0.7	1.0	1.4	0.9	0.4	<0.1
	8	<1	0.6	1.5	<0.1	0.4	1.0	0.8	1.2	0.2	<0.1
	9	<1	0.6	1.5	<0.1	0.2	0.7	0.8	1.0	0.1	<0.1
	10	<1	0.6	1.5	<0.1	0.1	0.7	0.5	1.2	0.1	<0.1
THA-4	1	<1	6.3	12.1	13.0	3.8	3.4	9.6	12.0	43.5	14.7
	2	<1	5.0	12.1	11.6	3.3	2.8	7.1	10.3	39.3	12.8
	3	<1	3.1	8.2	8.0	2.3	2.3	4.7	6.2	28.0	7.8
	4	<1	2.5	5.9	5.8	1.9	1.7	3.8	4.4	20.7	5.6
	5	<1	2.1	4.1	4.5	1.5	1.5	3.0	3.5	16.6	4.6
	6	<1	1.9	3.5	3.7	1.9	1.2	2.7	2.9	15.5	3.6
	7	<1	1.7	2.9	3.3	1.4	1.2	2.5	2.6	12.4	3.3
	8	<1	1.7	2.9	3.2	1.0	1.2	1.9	2.3	11.4	2.6
	9	<1	1.4	2.4	2.7	1.1	0.9	1.4	2.1	10.2	2.8
	10	<1	1.3	2.1	2.4	1.2	1.0	1.6	2.1	10.2	2.2
THA-4 in final H_2O aliquot ($\mu g/ml$)		<2	14	22	<2	<2	25	12	17	<2	<2

Table 25. *ELUTION OF CATIONS ADSORBED ON 25 mg Fe_2O_3 WITH 10 ml ALIQUOTS OF DISTILLED H_2O FOLLOWED BY 10 ml ALIQUOTS OF A SOLUTION OF 500 mg/l THA-1 OR THA-4*

Type and No. of aliquot		Cations leached from Fe_2O_3 (μg/ml)				
		Co^{+2}	Cu^{+2}	Ni^{+2}	Pb^{+2}	Zn^{+2}
H_2O*	1	2.7	2.6	1.4	5.2	2.1
	2	2.6	2.2	1.2	4.8	2.1
	3	2.6	2.2	1.2	5.1	2.0
	4	2.2	2.0	1.4	3.6	1.8
	5	2.1	1.7	1.3	3.0	2.2
	6	2.2	1.6	0.9	3.2	1.6
	7	1.8	1.3	0.9	2.1	1.8
	8	1.4	1.3	0.6	2.0	1.4
	9	1.4	1.5	0.3	1.8	1.2
	10	1.6	0.9	0.3	2.0	0.6
THA-1	1	12.6	17.3	12.0	49.7	16.7
	2	6.6	9.6	4.7	19.8	8.8
	3	2.9	5.5	2.6	9.3	4.6
	4	2.0	4.0	1.5	7.2	3.4
	5	2.1	3.2	0.6	5.4	3.0
	6	1.9	3.2	1.2	4.1	2.0
	7	2.1	3.4	0.8	3.0	2.4
	8	1.6	2.6	0.8	3.5	1.8
	9	1.2	2.8	0.5	2.0	1.6
	10	1.4	2.8	0.6	2.4	1.6
THA-4	1	16.4	17.6	12.0	43.5	14.7
	2	10.0	8.4	5.3	20.7	9.2
	3	7.4	5.2	3.2	11.4	4.9
	4	4.6	4.9	2.4	7.2	3.4
	5	3.6	3.2	2.8	5.6	2.6
	6	3.6	3.8	1.6	4.8	2.2
	7	3.4	2.6	0.8	3.2	2.8
	8	3.8	2.2	1.0	3.2	2.0
	9	3.2	2.4	0.6	3.0	1.6
	10	3.2	2.0	0.8	3.4	1.0

*Averages of H_2O runs preceding THA-1 and THA-4

Table 26. *ELUTION OF CATIONS ADSORBED ON 25 mg MONTMORILLONITE WITH 10 ml ALIQUOTS OF DISTILLED H_2O FOLLOWED BY 10 ml ALIQUOTS OF A SOLUTION OF 500 mg/l THA-1 OR THA-4*

Type and No. of aliquot	Cations leached from montmorillonite $(\mu g/ml)$				
	Co^{+2}	Cu^{+2}	Ni^{+2}	Pb^{+2}	Zn^{+2}
H_2O* 1	0.8	1.4	2.9	1.4	2.4
2	0.5	0.6	2.6	1.4	2.4
3	0.5	0.3	1.3	1.2	1.6
4	0.2	0.2	0.8	1.2	1.2
5	0.2	0.1	0.6	1.2	0.8
6	0.2	0.1	0.3	1.3	0.3
7	<0.1	0.1	0.2	1.0	0.2
8	<0.1	0.1	<0.1	0.8	0.2
9	<0.1	0.1	<0.1	0.8	0.2
10	<0.1	0.1	<0.1	0.8	0.2
THA-1 1	9.8	15.9	13.2	52.8	14.7
2	4.5	7.8	6.8	33.1	9.2
3	2.6	4.3	3.5	18.6	4.9
4	1.8	2.8	2.6	13.5	2.9
5	1.6	2.5	2.0	12.4	2.6
6	1.6	2.0	1.8	10.4	2.2
7	1.5	2.1	1.5	9.3	2.0
8	1.4	1.8	1.2	7.3	2.2
9	1.1	1.4	1.2	6.2	1.6
10	0.9	1.4	1.2	5.2	1.2
THA-4 1	12.2	18.0	12.0	49.7	15.4
2	6.5	11.1	6.2	25.9	8.2
3	3.8	6.0	3.8	13.4	4.9
4	2.3	3.6	2.6	9.3	5.4
5	1.5	2.8	1.8	7.2	3.0
6	1.5	2.4	1.5	6.2	2.6
7	1.3	2.4	1.6	6.5	1.5
8	1.5	1.4	1.2	4.2	2.0
9	1.0	1.2	1.2	4.8	1.3
10	1.0	1.2	1.2	3.3	0.6

*Averages of H_2O runs preceding THA-1 and THA-4