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CHEMISTRY OF GOLD-HUMIC INTERACTIONS

D.J. Gray, M.J. Lintern and G.D. Longman

CRC LEME OPEN FILE REPORT 43

September 1998

(CSIRO Division of Exploration Geoscience Report I28R, 1990.
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RESEARCH ARISING FROM CSIRO/AMIRA REGOLITH GEOCHEMISTRY PROJECTS 1987-1993

In 1987, CSIRO commenced a series of multi-client research projects in regolith geology and geochemistry which were sponsored by companies in the Australian mining industry, through the Australian Mineral Industries Research Association Limited (AMIRA). The initial research program, "Exploration for concealed gold deposits, Yilgarn Block, Western Australia" (1987-1993) had the aim of developing improved geological, geochemical and geophysical methods for mineral exploration that would facilitate the location of blind, buried or deeply weathered gold deposits. The program included the following projects:

P240: Laterite geochemistry for detecting concealed mineral deposits (1987-1991). Leader: Dr R.E. Smith.
Its scope was development of methods for sampling and interpretation of multi-element laterite geochemistry data and application of multi-element techniques to gold and polymetallic mineral exploration in weathered terrain. The project emphasised viewing laterite geochemical dispersion patterns in their regolith-landform context at local and district scales. It was supported by 30 companies.

P241: Gold and associated elements in the regolith - dispersion processes and implications for exploration (1987-1991). Leader: Dr C.R.M. Butt.

The project investigated the distribution of ore and indicator elements in the regolith. It included studies of the mineralogical and geochemical characteristics of weathered ore deposits and wall rocks, and the chemical controls on element dispersion and concentration during regolith evolution. This was to increase the effectiveness of geochemical exploration in weathered terrain through improved understanding of weathering processes. It was supported by 26 companies.

These projects represented "an opportunity for the mineral industry to participate in a multi-disciplinary program of geoscience research aimed at developing new geological, geochemical and geophysical methods for exploration in deeply weathered Archaean terrains". This initiative recognised the unique opportunities, created by exploration and open-cut mining, to conduct detailed studies of the weathered zone, with particular emphasis on the near-surface expression of gold mineralisation. The skills of existing and specially recruited research staff from the Floreat Park and North Ryde laboratories (of the then Divisions of Minerals and Geochemistry, and Mineral Physics and Mineralogy, subsequently Exploration Geoscience and later Exploration and Mining) were integrated to form a task force with expertise in geology, mineralogy, geochemistry and geophysics. Several staff participated in more than one project. Following completion of the original projects, two continuation projects were developed.

P240A: Geochemical exploration in complex lateritic environments of the Yilgarn Craton, Western Australia (1991-1993). Leaders: Drs R.E. Smith and R.R. Anand.

The approach of viewing geochemical dispersion within a well-controlled and well-understood regolith-landform and bedrock framework at detailed and district scales continued. In this extension, focus was particularly on areas of transported cover and on more complex lateritic environments typified by the Kalgoorlie regional study. This was supported by 17 companies.

P241A: Gold and associated elements in the regolith - dispersion processes and implications for exploration. Leader: Dr. C.R.M. Butt.

The significance of gold mobilisation under present-day conditions, particularly the important relationship with pedogenic carbonate, was investigated further. In addition, attention was focussed on the recognition of primary lithologies from their weathered equivalents. This project was supported by 14 companies.

Although the confidentiality periods of the research reports have expired, the last in December 1994, they have not been made public until now. Publishing the reports through the CRC LEME Report Series is seen as an appropriate means of doing this. By making available the results of the research and the authors' interpretations, it is hoped that the reports will provide source data for future research and be useful for teaching. CRC LEME acknowledges the Australian Mineral Industries Research Association and CSIRO Division of Exploration and Mining for authorisation to publish these reports. It is intended that publication of the reports will be a substantial additional factor in transferring technology to aid the Australian Mineral Industry.

This report (CRC LEME Open File Report 43) is a Second impression (second printing) of CSIRO, Division of Exploration Geoscience Restricted Report 128R, first issued in 1990, which formed part of the CSIRO/AMIRA Project P241.

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PREFACE

The chemistry of Au - Humic interactions - in particular how Au is bonded to soluble, and insoluble, humic matter, and how this is related to solution conditions - is an important area of Au geochemistry. Understanding of this field is important in terms of work within the Weathering Processes Research Group on how soil Au anomalies are formed and how to use soil as an exploration medium. Specifically, the study:

- (i) demonstrates that Au reacts with various humate solutions to form stabilized Au sols, as has been observed by other workers;
- (ii) shows that the so-formed Au sol is readily broken down or modified by addition of other ligands;
- (iii) indicates that light may have a role in the formation of such Au-humate species.

This investigation is complementary to other investigations of Au chemistry and studies of the nature and surface expression of gold mineralization. Together they address many of the principal objectives of the Project.

C.R.M. Butt,
Project Leader.
November, 1990

ABSTRACT

This report describes experiments on the interaction of ionic Au with various sources of soluble humic acid. The concentrations of soluble ($< 0.45 \mu\text{m}$) Au in the presence of humic phases were dependant on a number of factors, including Au concentration, humic concentration, humic source, and the presence or absence of light. Such variations in solubility can readily explain the wide divergence of opinion on the effect of soluble humic phases on Au solubility, as detailed in the report.

Results obtained here indicated that the Au formed a very fine, highly coloured sol, in agreement with other work on the interaction of Au with humic phases (Ong and Swanson, 1969; Fedoseyeva *et al.*, 1986) and with other organic molecules (Fabrikanos *et al.*, 1963). Formation of the sol is activated by light, in agreement with previous work (Fabrikanos *et al.*, 1963).

The Au sol is effectively decolourized by the addition of ligands with strong (CN^-) or moderate (I^- , $\text{S}_2\text{O}_3^{2-}$, SCN^-) affinities for Au, or by ligands with weak (Cl^-) affinities for Au when in high concentration. This suggests that the Au sol will only be stable in the absence of such ligands. As the unpurified humate preparations readily converted Au to the sol, rather than complexing it, these preparations do not contain significant concentrations of such Au ligands.

It is postulated that the colour of the Au sol, rather than just indicating the size of the Au particle, may be due to specific chemical factors. Thus, a further understanding of the mechanism of the colour of this phase could give further important information on the chemistry of Au in the presence of humic material.

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LIST OF ABBREVIATIONS

Asc	ascorbic acid
CN ⁻	cyanide
EDTA	ethylenediamminetetraacetic acid
E_{\max}	molar absorbtivity (measured in $M^{-1}.cm^{-1}$), which is a measure of the absorbance per mole per cm of light path
HCl	hydrochloric acid
HNO ₃	nitric acid
I ⁻	Iodide
mM	millimoles/litre
<u>M</u>	moles/litre
NaOH	sodium hydroxide
OC	Organic Carbon
S ₂ O ₃ ²⁻	Thiosulphate
SCN ⁻	Thiocyanate
UV	ultra-violet

1. Introduction

As detailed in Gray (1988), the chemistry of the interactions of Au with soluble organic matter has been under investigation for over half a century, but is still poorly understood. Various workers have published results indicating that soluble organic matter dissolves Au (Freise, 1931; Baker, 1973, 1978; Boyle *et al.*, 1975, Varshal *et al.*, 1984), precipitates Au (Fetzer, 1934, 1946), or forms stabilized colloids with Au (Ong and Swanson, 1969; Fedoseyeva *et al.*, 1986). The reasons for these contradictory results may include differences in experimental procedures and/or different sources of organic materials. For example, if high concentrations of Au and organic matter are reacted together then Au may be reduced and precipitated by the organic phase, whereas at low concentrations, organic acids could tend to complex the Au and thus maintain it in solution. However, there still remains a clear need for an understanding of how Au and humic matter interact, which could then be used to reassess this previous work.

It is important to ascertain the chemistry of the organic phases interacting with Au (and other metals). Organic Matter is usually divided into two groups (Schnitzer and Khan, 1972):

- (i) non-humic substances: compounds that have recognizable chemical characteristics, such as carbohydrates, proteins and other low molecular weight organic substances. In general, these compounds are relatively easily attacked by micro-organisms in the soil and have a relatively short survival rate. This group includes compounds such as cyanide or amino acids, which are demonstrated to have major, and chemically understood, abilities to dissolve Au (Smith and Hunt, 1985; Korobushkina *et al.*, 1983; and other references listed in Gray, 1988);
- (ii) humic substances: these are amorphous, brown or black, hydrophilic, acidic, polydisperse substances of molecular weights ranging from several hundreds to tens of thousands. Humic substances are normally divided into three main fractions (Felbeck, 1971):-
 - a. *humic acid*, which is soluble in dilute alkaline solution, but is precipitated by acidification ($\text{pH} < 1$),
 - b. *fulvic acid*, which remains in the aqueous acidified solution, and
 - c. *humins*, which cannot be extracted by dilute base or acid.

The interactions of humic substances with Au are still poorly understood, and as detailed above, subject to some controversy. Thus, further investigations have been performed, as detailed in this report, which may cast some light on the various disputes described above.

Humic acid is deprotonated in neutral to alkaline solutions, and therefore is more properly denoted as humate ion in these conditions. The specific chemistry of the Au-humate interaction is of importance, as soluble organic matter is commonly in high concentrations in many soil solutions and surface waters. It is important to see how strongly humate and/or fulvate may complex Au, relative to other molecules. In addition, the chemistry of the bonding between soluble humate and Au may be similar to the bonding between solid organic matter and Au. Thus, a study on the interactions between soluble humate and Au may give information both on solution controls on Au, and on how Au may be precipitated in organic-rich soils or soil horizons.

2. Humate Materials

Three different soluble organic matter solutions were used:

- (i) Humate 1: Aldrich Humic Acid, sodium salt, tech. (cat. no. H1,675-2). This is a "Standard" Humic Acid, as described in Section 1. Properties of this material are detailed in MacCarthy and Malcolm (1987);
- (ii) Humate 2: fresh *Eucalyptus* spp. leaves were collected and immersed in deionized water for 12 months. The solution was then filtered through 0.45 μm membrane filter.
- (iii) Humate 3: fresh *Eucalyptus* spp. twigs were collected and immersed in deionized water for 12 months. The solution was then filtered through 0.45 μm membrane filter.

The humate 2 and 3 solutions were intended as an empirical model for solutions resulting from decaying plant material, and were not chemically separated as detailed in Section 1.

3. Experimental Studies

3.1. Analytical Methods

The three humate solutions were analysed for organic carbon (OC) content, using a modification of the method of McCleod (1975). Five mL of concentrated humate solution was mixed with 10 mL 0.167 mole/litre (M) potassium dichromate and then 20 mL concentrated sulphuric acid added. After 15 min 5 mL concentrated phosphoric acid, 30 mL deionized water and 5 drops orthophenanthroline indicator were added and the solution titrated against standardized ferrous sulphate solution (about 0.4 M). The OC content was calculated from the amount of dichromate consumed.

Note that the humate concentration is measured in mg/L of OC in this report, so as to allow direct comparisons between the three different humate solutions, and particularly humate 2 and humate 3, which had only been isolated as solutions. Humate 1 was calculated as containing 64% OC: *i.e.*, 640 mg/L OC corresponds to 1000 mg/L humate 1 on a total weight basis.

Adsorption Spectra were taken using a Varian DMS 80 UV Visible Spectrophotometer, with optically matched one cm silica optical cells. Data was outputted to computer, using an analog-digital converter and in-house programs, to enable comparison between spectra. The spectrum of a solution is the measure of the light absorbance ¹ of a solution vs. wavelength. Thus, in Fig. 3 for example, the 80 day solution is virtually

¹ Absorbance is a specific measure of light absorption, given by:

transparent (absorbance < 0.02) to light of wavelengths greater than 700 nm (the red end of the spectrum) and shows increased light absorption at 350 nm and beyond (the ultra-violet end of the spectrum).

3.2. Experiment A

3.2.1. Methods

Gold - humate mixtures were prepared so as to test the effect of concentration and light on the chemistry of Au humate mixtures. Specified amounts of Au chloride, in 1 M hydrochloric acid (HCl), were added to humate 1 solutions. The solutions were then taken to pH 7 with sodium hydroxide (NaOH) and stored in glass, with intermittent shaking.

The particular mixtures used in Experiment A were:

Sample 100light: 100 mg/L Au / 64 mg/L Humate 1², in the light;

Sample 100dark: 100 mg/L Au / 64 mg/L Humate 1, in the dark;

Sample 10light: 10 mg/L Au / 6.4 mg/L Humate 1, in the light;

Sample 10dark: 10 mg/L Au / 6.4 mg/L Humate 1, in the dark.

At specified time intervals 2 mL aliquots of the suspensions were taken (immediately after shaking) and filtered through 5 μm membrane filter. The resulting filtrate was then filtered through 0.45 μm membrane filter. The 0.45 μm membrane and the filtrate were then separately digested with aqua-regia, made up to 10 mL with 1 M HCl / 0.3 M nitric acid (HNO_3), and analysed for Au on a Varian AA-875 Atomic Absorption Spectrophotometer using flame excitation. The concentration of Au in the $>5 \mu\text{m}$ fraction was obtained by difference.

As a rough approximation the three fractions can be described as:

$<0.45 \mu\text{m}$: soluble;

$0.45 - 5 \mu\text{m}$: colloidal;

$>5 \mu\text{m}$: precipitated.

$$\text{Absorbance} = \log (P_0/P)$$

where P_0 = Intensity of incident light beam (at a particular wavelength)

P = Intensity of light beam transmitted through the solution.

The reader is recommended to any standard text on Spectrophotometry (*e.g.*, Fritz and Schenk, 1979, p. 69) if further details are required.

² Note that, as discussed in Section 2.1, humate concentration is being measured in OC content per volume rather than as weight per volume.

Note, however, that the $<0.45 \mu\text{m}$ fraction, though generally considered the soluble fraction, may still contain species that are large at a molecular level, such as organic molecules and or Au aggregates.

At specified time intervals aliquots of the suspensions were taken from settled suspensions and the light absorption spectra taken.

3.2.2. Gold Concentrations in the Various Solution Fractions

Distribution of the Au for the various size fractions is shown in Table 1 and illustrated diagrammatically in Figs. 1 and 2.

Table 1: Distribution of Gold in Particle Size Fractions of Experiment A Suspensions.

Sample	[Au]* (mg/L)	[Humate 1] (mg/L)	Treatment	Time (days)	Au concentration in each fraction		
					$<0.45 \mu\text{m}$	$0.45 - 5 \mu\text{m}$	$>5 \mu\text{m}^\#$
100light	100	64	Light	9	9.7	60.5	28.8
				28	20.7	42.9	36.4
				60	16.9	75.5	7.6
100dark	100	64	Dark	9	10.5	8.4	81.1
				28	16.8	30.5	52.7
				60	10.5	30	59.5
10light	10	6.4	Light	9	10.5	0	0
				28	10.8	1.2	0
				60	8	0	2
10light	10	6.4	Dark	9	2	6.9	1.1
				28	8.2	0.3	1.5
				60	5.3	0.7	4

* [] denotes concentration.

calculated by difference.

The ratio between Au and humate 1 is the same for all four suspensions, and differ only in terms of the absolute concentrations. However, the size distribution of Au is dramatically different (Table 1; Figs. 1 and 2) for each suspension. In 100light, a maximum of 20% of the total Au (20 mg/L Au) is found in the $<0.45 \mu\text{m}$ fraction of the suspension, and there was a clearly visible black precipitate (presumably of precipitated Au), whereas in 10light, 80 to 100% of the total Au (8 - 10 mg/L Au) is in the $<0.45 \mu\text{m}$ fraction and the solution is clear of any solids. A similar comparison can be made between 100dark and 10dark. Additionally, a major proportion of the Au (up to 75%) in 100light and 100dark is found within the $0.45 - 5 \mu\text{m}$ fraction. These experiments alone do not reveal whether the lower proportion of Au in the $<0.45 \mu\text{m}$ fraction of the 100 mg/L Au samples is due to the higher level of Au or of the humate 1 (discussed further in Section 3.3), but appear to suggest an absolute limit in the solubility of Au under these conditions of about 10 - 20 mg/L.

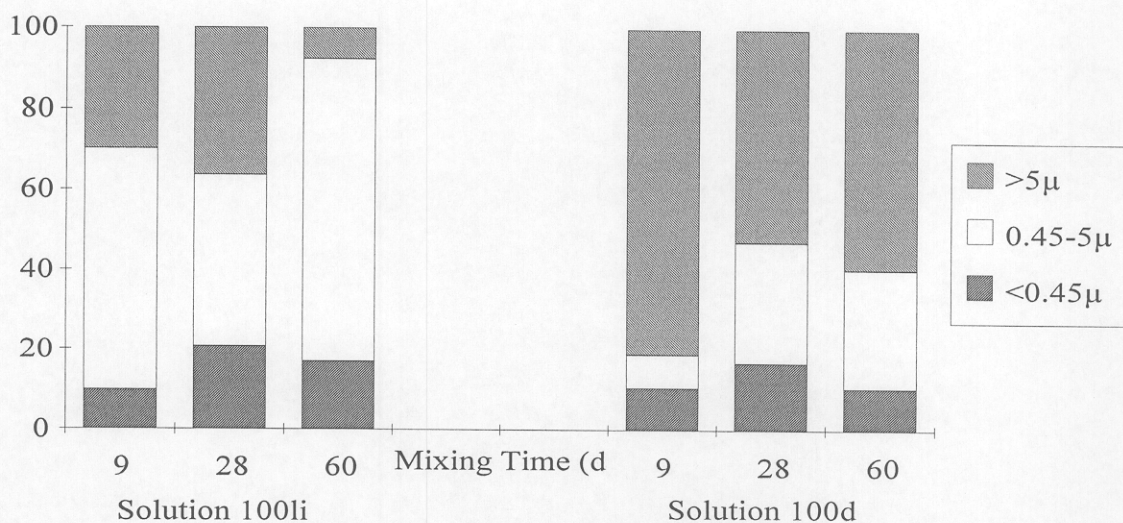


Figure 1: Distribution of Au in Solutions 100light (100 mg/L Au / 64 mg/L Humate 1 / Light) and 100dark (100 mg/L Au / 64 mg/L Humate 1 / Dark), vs. Time.

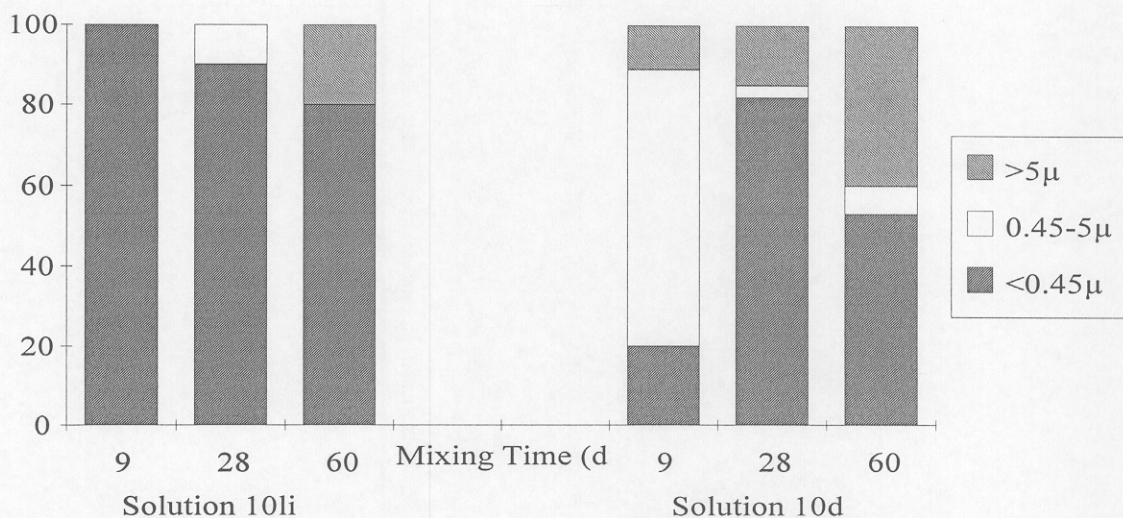


Figure 2: Distribution of Au in Solutions 10light (10 mg/L Au / 6.4 mg/L Humate 1 / Light) and 10dark (10 mg/L Au / 6.4 mg/L Humate 1 / Dark), vs. Time.

The distribution of Au is strongly influenced by the presence or absence of light. Comparison of solution 10light with 10dark (Table 2; Fig. 2), indicates that significantly less of the Au in solution 10dark is in the $< 0.45 \mu\text{m}$ fraction. In addition, there are significant changes with time in the distribution of Au in the finer fractions in solution 10dark, with the proportion of Au in the $< 0.45 \mu\text{m}$ fraction increasing from 20% to 80% from 9 to 28 days. One feasible hypothesis is that Au in the $< 0.45 \mu\text{m}$ fraction is in a phase whose formation is activated by light. Thus, the darkened sample may take longer to form this species. In addition, the final concentration of Au in the $< 0.45 \mu\text{m}$ fraction may be reduced from that observed for solution 10light (Fig. 2) due to irreversible precipitation of Au by reactions occurring prior to Au-humate species formation. As will be described later (Section 3.2.3), this hypothesis is also supported by the spectrophotometric results.

Qualitatively similar differences were observed for the 100 mg/L case. The concentrations of Au in the $< 0.45 \mu\text{m}$ and $0.45 - 5 \mu\text{m}$ fractions of solution 100dark were significantly lower than for 100light (Fig. 1). In addition, the concentration of Au in these fractions of solution 100dark showed a general increase with time (Fig. 1), though not to the same degree as 10dark (Fig. 2).

3.2.3. Spectrophotometry of Experiment A Solutions

Use of spectrophotometry to investigate Au humate chemistry is useful, because:

- (i) it offers a quantifiable measure of colour, which may be related to concentration of a particular species;
- (ii) variation in the positions of absorption peaks can be measured;
- (iii) the presence of light-absorbing species can be tested even where the colour is obscured by high concentrations of organic matter in the solutions.

Visible absorption spectra for solution 100light were taken at 2, 8, 37 and 80 days (Fig. 3). The most marked feature of these spectra is the absorption peak at about 530 nm in the 2 day spectrum, resulting in the solution being pink to the human eye. This peak appears to diminish with time. As will be discussed below, this absorption peak is diagnostic for a Au metal sol. Solution 100dark does not show this absorption peak (Fig. 4). Thus, these results suggest that there is an initial formation of Au sol that is activated by light. Over time this phase is broken down or precipitated.

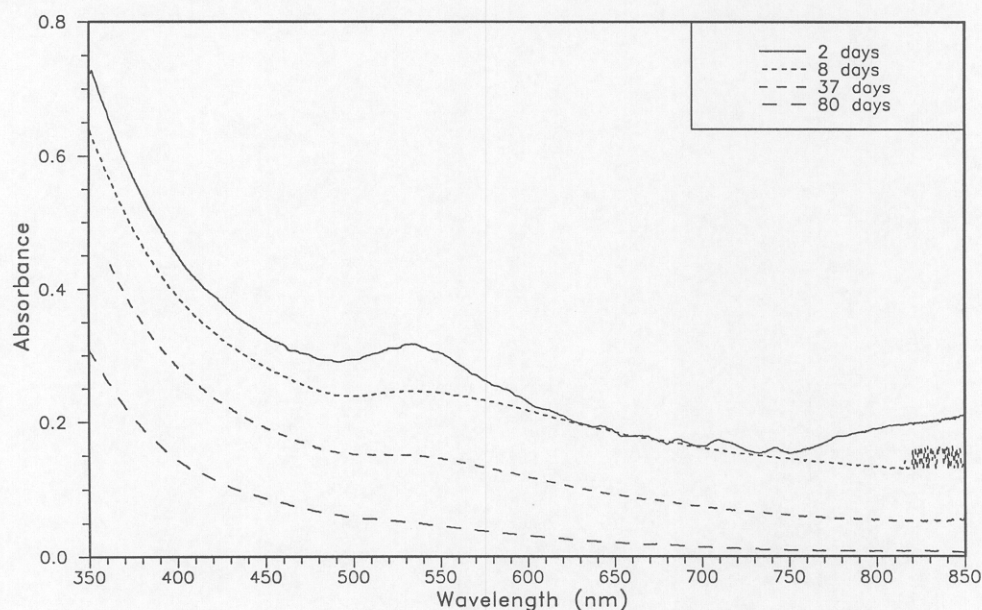


Figure 3: Absorption Spectra of Solution 100light at 2, 8, 37 and 80 days.

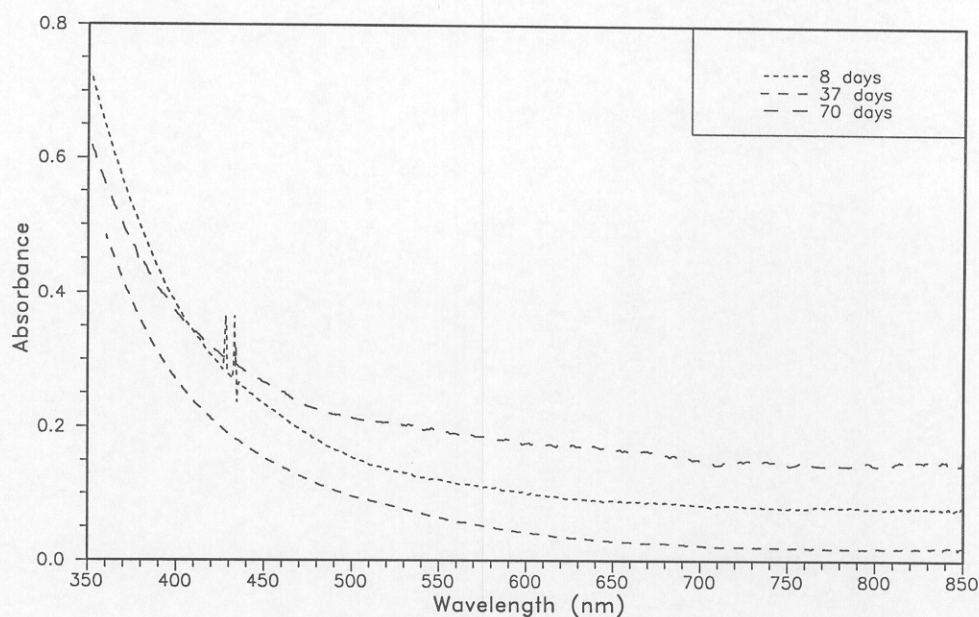


Figure 4: Absorption Spectra of Solution 100dark at 8, 37 and 80 days.

The 530 nm absorption peak can be clearly observed in the spectrum of solution 10light (Fig. 5). The absorption peak is observed at 2 days as a broad peak centered at about 540 nm. At 8 days, the peak is sharper and shifted to about 525 nm, finally stabilizing at about 520 nm after 37 days. Note that the intensity of the peak is almost as high as the initial absorption band observed for solution 100light (Fig. 3), despite the total concentration of Au in 100light being 10 times higher, presumably because only about 10 to 20% of the Au in solution 100light is as the Au sol, with the rest being as colloidal or precipitated Au (Fig. 1).

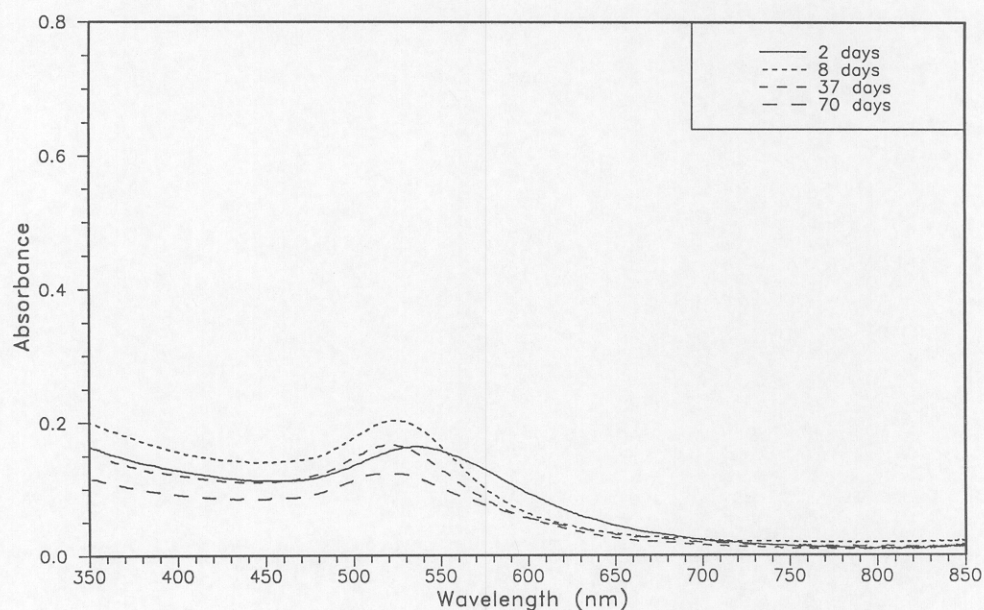


Figure 5: Absorption Spectra of Solution 10light at 2, 8, 37 and 80 days.

As a consequence of this high absorbance around 530 nm, the solution has the pink-purple colour typical of a "Au sol": *i.e.*, Au present as very fine (<50 nm) particles of reduced Au. This visible light absorption for the Au humate solutions contrasted strongly with Au at the same concentration in a chloride solution (Fig. 26), which is colourless. Other species, such as AuI_2^- , $\text{Au}(\text{S}_2\text{O}_3)_2^{3-}$ and $\text{Au}(\text{CN})_2^-$ are also virtually colourless at these Au concentrations.

Thus, the presence of a similar 530 nm absorption peak in the 100light spectra (Fig. 1) indicates that, at least initially, a significant proportion of the Au in this system had formed a Au sol. Over time, this peak disappeared, indicating that the Au sol was being removed from solution, possibly via decomposition or precipitation of the sol.

Unfortunately, the spectrum of solution 10dark was not taken at 2 days, because of equipment failure. However, visual inspection of the two solutions at this time showed major differences: solution 10light was a clear pink-purple colour (due to the major light absorption at 550 nm and below, whereas solution 10dark was virtually colourless, *i.e.*, had little visible light absorption. Obviously, the 550 nm absorption peak had not developed in solution 10dark at 2 days. At 8 days and afterwards, the light absorption characteristics of solution 10dark (Fig. 6) was very similar to that of 10light, both in terms of the measured absorption spectra and the observed colour. Thus, formation of the pink Au-humate species is delayed but not stopped by the absence of light.

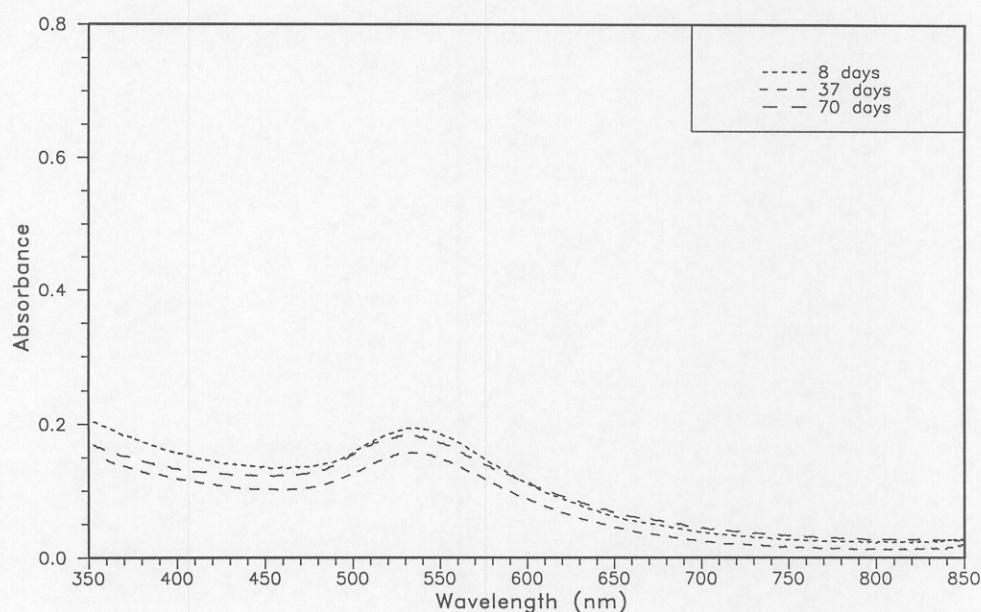


Figure 6: Absorption Spectra of Solution 10dark at 8, 37 and 80 days.

Results from this experiment demonstrate that the distribution of Au between various particle sizes is strongly influenced by the absolute concentration of the Au and/or humate, and also by the presence or absence of light. Spectrophotometric evidence suggests that Au forms a metal sol in the presence of the humate. Formation of this species is enhanced in the presence of light, and the species is formed quickly in solutions 100light and 10light. In solution 100light the Au sol then decomposes with time.

3.3. Experiment B

3.3.1. Methods

Experiment B involved 30 separate solutions prepared by adding a specified amount of Au solution to various humate solutions. The solutions were then taken to pH 7 with NaOH solution, and stored in glass, with intermittent shaking.

Nine different humate/Au solutions were prepared for each different humate type (Section 2), using three differing humate concentrations, namely:

Humate 1:	640 mg/L, 64 mg/L and 6.4 mg/L;
Humate 2:	1300 mg/L, 130 mg/L and 13 mg/L;
Humate 3:	250 mg/L, 25 mg/L and 2.5 mg/L;

and three different Au concentrations, namely:

10 mg/L, 1 mg/L and 0.1 mg/L.

Thus, the Au:Humate ratio for each of the different humate solutions varied by 4 orders of magnitude (*e.g.*, from 10 mg/L Au / 6.4 mg/L OC to 0.1 mg/L Au / 640 mg/L OC for Humate 1). Three additional solutions were prepared with 10, 1 and 0.1 mg/L Au, but without any humate added. A list of the various solutions is given in Table 2.

The samples were left in the light for two weeks, in order to activate formation of the Au-humate species (Section 3.2), and then stored in the dark for another 2½ months. At this stage, 2 mL aliquots of the suspensions were taken (immediately after shaking) and filtered through 5 µm membrane filter. The resulting filtrate was then filtered through 0.45 µm membrane filter. The 0.45 µm membrane filter and the final filtrate were then separately digested with aqua-regia, made up to 10 mL with 1 M HCl / 0.3 M HNO₃, and analysed for Au on a Varian AA-875 Atomic Absorption Spectrophotometer, using flame excitation. Solutions with Au concentration less than 60 µg/L were re-analysed by ICP-MS.

At specified time intervals, aliquots were taken from settled suspensions and the spectra taken (Section 3.1). Differential patterns were obtained by mathematical subtraction of a sample spectra from a reference spectra, with additional correction for background dispersion.

3.3.2. Distribution of Gold

The distributions of Au in the various size fractions of the suspensions are given in Table 2, and are illustrated diagrammatically in Figs. 7- 15

Table 2: Distribution of Gold in Particle Size Fractions of Experiment B Suspensions.

Organic Matter used	Organic Carbon (mg/L)	Au added (mg/L)	Au concentration in size fractions		
			<0.45 μ m	0.45-5 μ m	>5 μ m*
Humate 1	640	10	9050	200	750
		1	1100	45	0
		0.1	160	5	0
	64	10	9450	75	475
		1	1000	20	0
		0.1	145	5	0
	6.4	10	8750	205	1045
		1	950	15	35
		0.1	150	2.5	0
Humate 2	1300	10	900	1050	8050
		1	180	45	775
		0.1	170	5	0
	130	10	3950	300	5750
		1	445	20	535
		0.1	95	15	0
	13	10	5450	135	4415
		1	320	2.5	678
		0.1	65	2.5	32
Humate 3	250	10	9500	225	275
		1	900	75	25
		0.1	115	10	0
	25	10	8850	450	700
		1	1000	15	0
		0.1	140	10	0
	2.5	10	5300	1950	2750
		1	600	75	325
		0.1	170	10	0
No Humate		10	9000	85	915
		1	275	65	660
		0.1	140	10	0

* calculated by subtracting total Au from the Au in the two finer fractions.

Note that there is a systematic error for the 0.1 mg/L Au suspensions, probably due to analytical inaccuracies at the lower Au concentrations, with the <0.45 μ m fraction commonly containing significantly more Au than was originally added. This occurs even for humate 1, which is unlikely to have high Au concentrations, and in the blanks, to which no humate was added. Therefore, though the 0.1 mg/L Au data could be used to observe gross changes (*i.e.*, the 13 mg/L humate 2 / 0.1 mg/L Au sample clearly has little Au in the <0.45 μ m fraction), they should generally be used with caution.

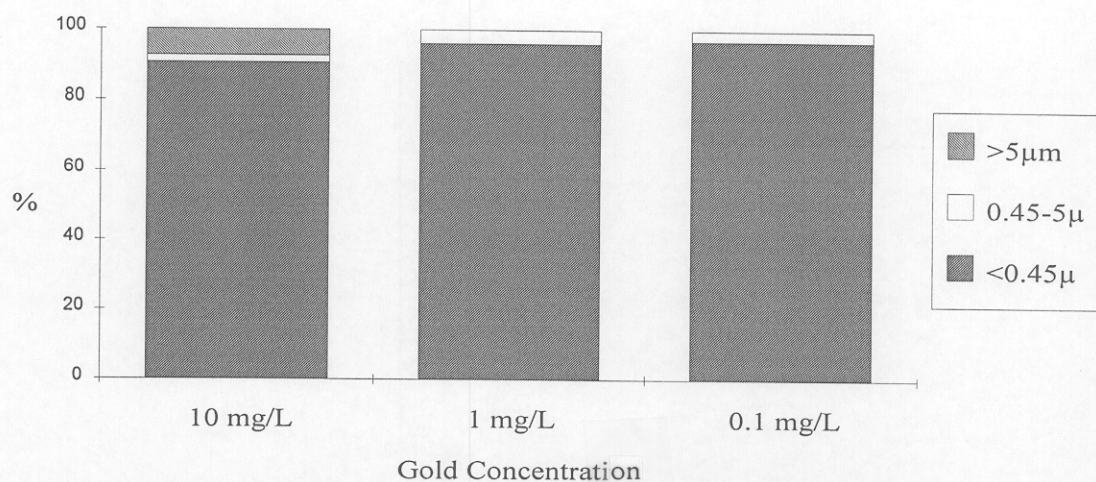


Figure 7: Distribution of Gold in Varying Concentrations in Suspensions with 640 mg/L Humate 1.

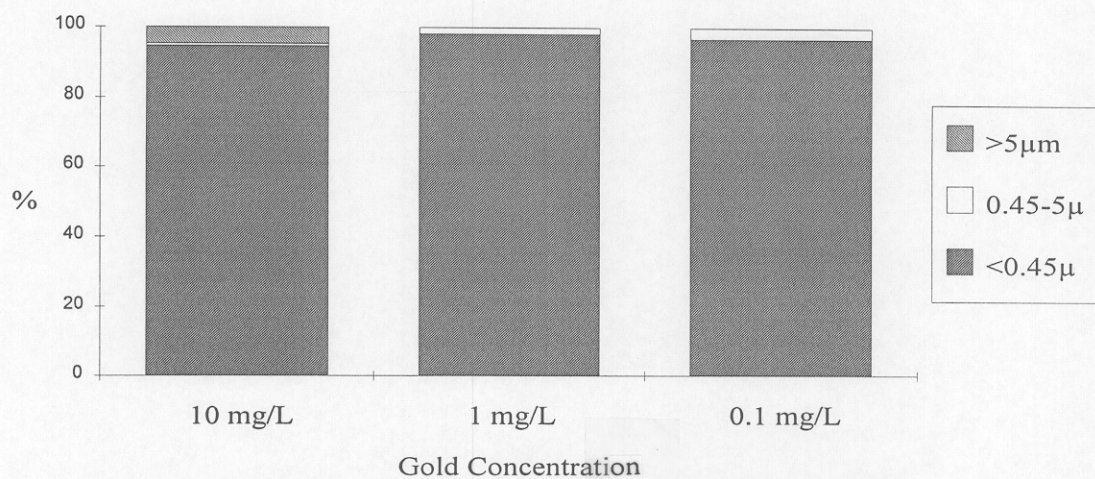


Figure 8: Distribution of Gold in Varying Concentrations in Suspensions with 64 mg/L Humate 1.

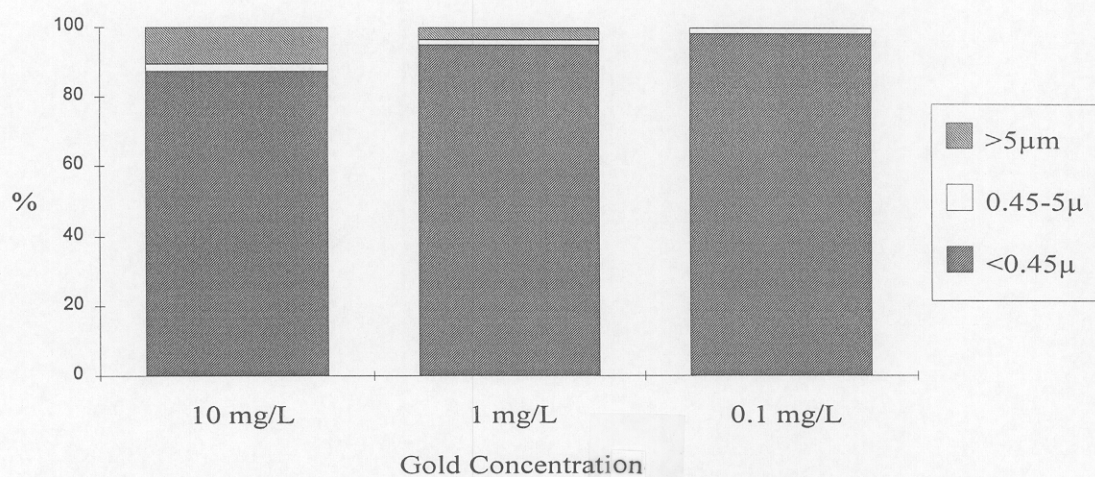


Figure 9: Distribution of Gold in Varying Concentrations in Suspensions with 6.4 mg/L Humate 1.

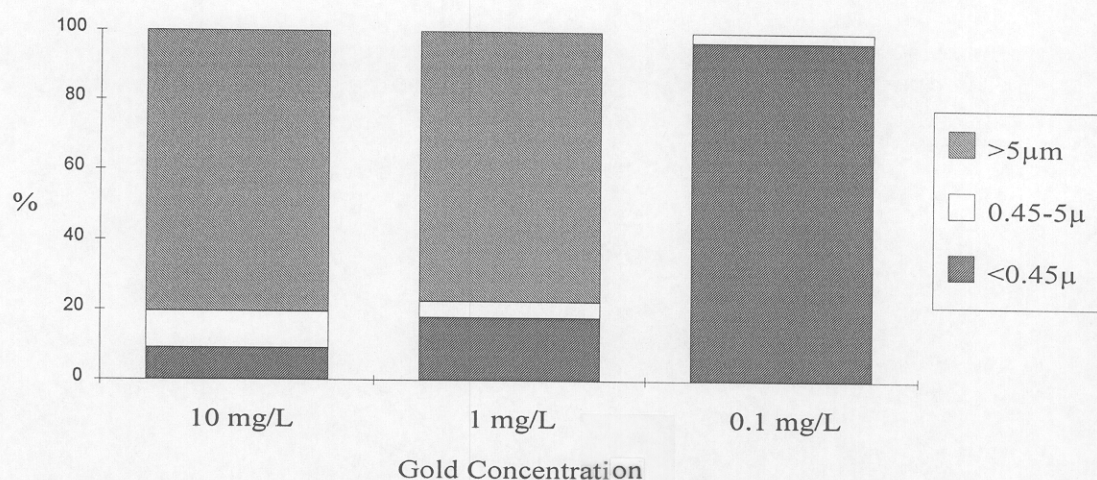


Figure 10: Distribution of Gold in Varying Concentrations in Suspensions with 1300 mg/L Humate 2.

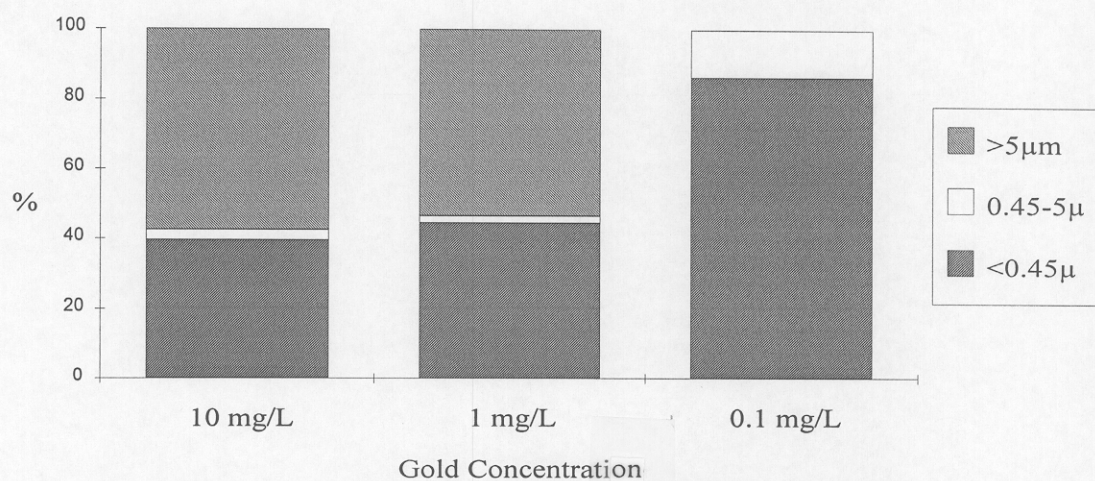


Figure 11: Distribution of Gold in Varying Concentrations in Suspensions with 130 mg/L Humate 2.

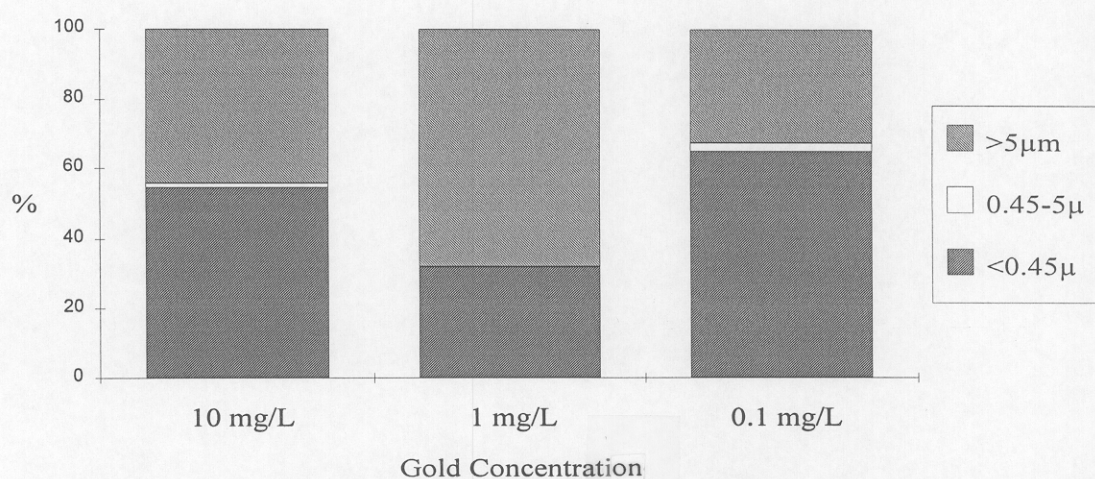


Figure 12: Distribution of Gold in Varying Concentrations in Suspensions with 13 mg/L Humate 2.

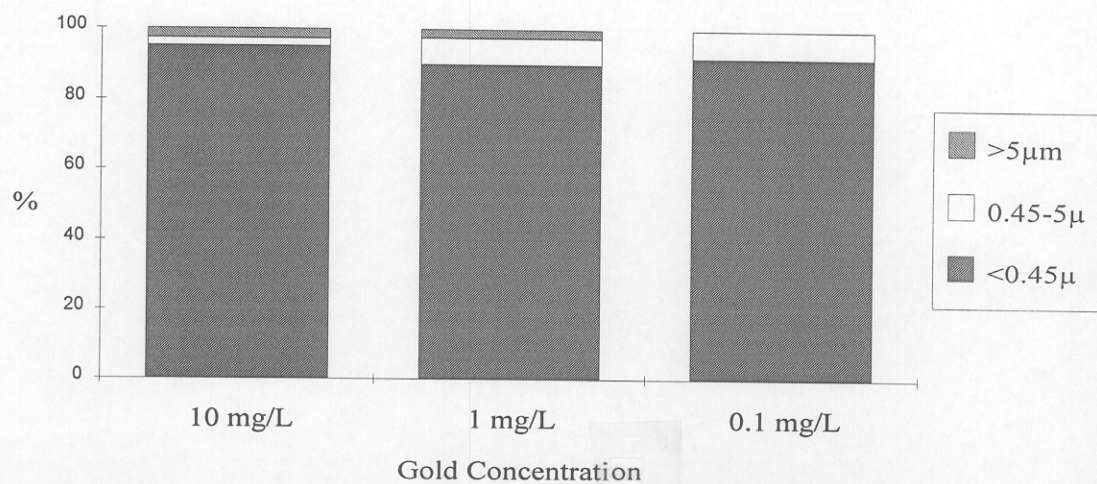


Figure 13: Distribution of Gold in Varying Concentrations in Suspensions with 250 mg/L Humate 3.

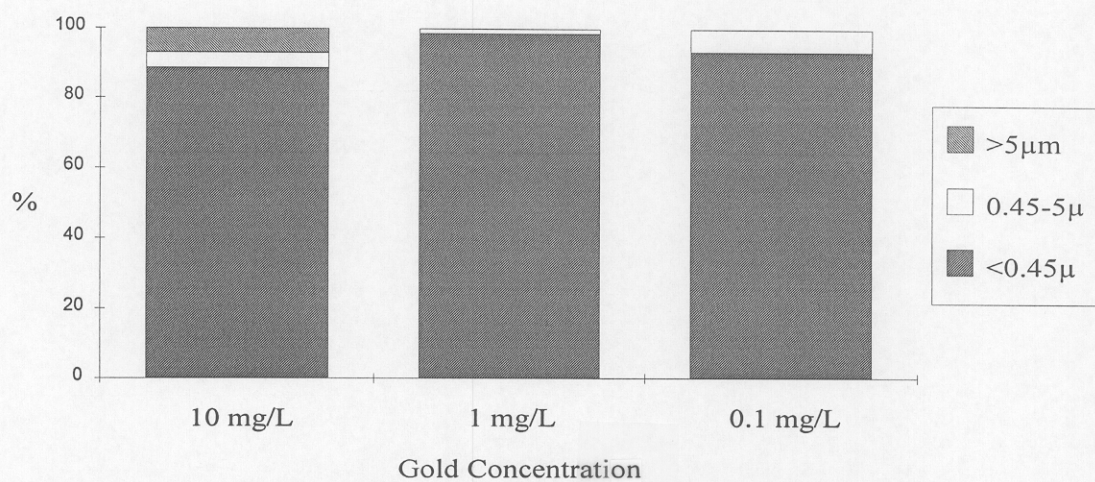


Figure 14: Distribution of Gold in Varying Concentrations in Suspensions with 25 mg/L Humate 3.

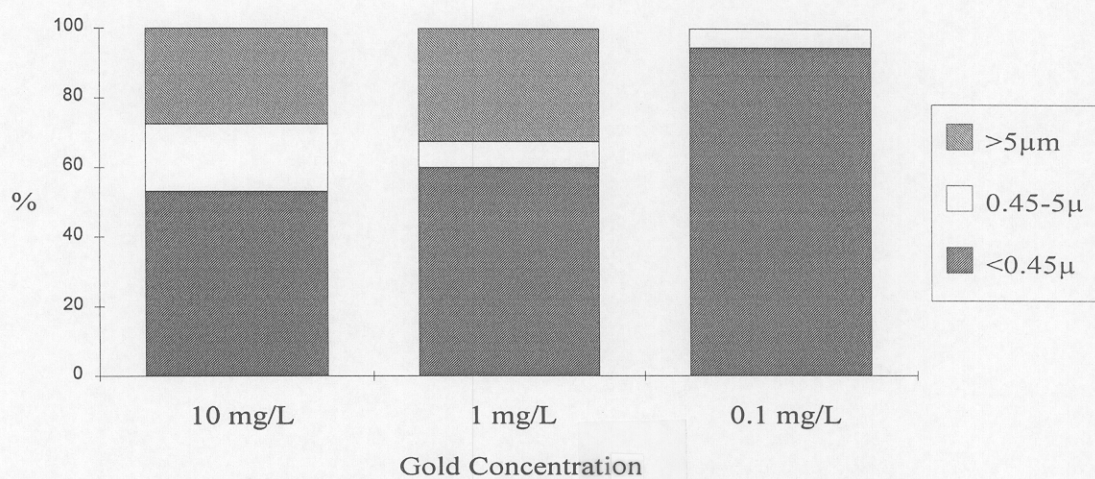


Figure 15: Distribution of Gold in Varying Concentrations in Suspensions with 2.5 mg/L Humate 3.

Data for the size distribution of Au in the humate 1 mixtures (Table 2; Figs. 7- 9) indicate that Au is generally soluble (*i.e.*, $< 0.45 \mu\text{m}$) in the presence of various humate 1 concentrations (6.4 to 640 mg/L), over a range of Au concentrations (0.1 to 10 mg/L). Results for solution 100light (from Experiment A; Section 3.2.2; Fig. 1) indicates that this high relative solubility of Au decreases dramatically at a Au concentration of 100 mg/L (where the humate 1 concentration is 64 mg/L). Thus, the lower proportion of Au in the $<0.45 \mu\text{m}$ fraction of solution 100light suggests an upper limit for Au solubility of about 10 to 20 mg/L in a 64 mg/L humate 1 solution.

Results for humate 2 (Figs. 10 - 12) show more complex interactions. For Au concentrations of both 10 mg/L and 1 mg/L, the proportion of Au in the $<0.45 \mu\text{m}$ fraction INCREASED with DECREASING humate 2 concentrations. Thus, at high concentrations humate 2 is acting to precipitate Au.

Humate 3 (Figs. 13 - 15) appears to behave similarly to humate 1. At 250 and 25 mg/L humate 3 (Figs. 13 and 14), over 90% of the Au is in the $<0.45 \mu\text{m}$ fraction. However, there is a significant reduction in the proportion of the Au in the $<0.45 \mu\text{m}$ fraction when the humate 3 concentration is reduced to 2.5 mg/L (Fig. 15). This concentration is about $2\frac{1}{2}$ times lower than the lowest humate 1 concentration (Fig. 9), for which there was no visible reduction in Au solubility. This effect could represent a saturation of the available sites for interaction of the Au in the low humate solutions.

In summary, these results show that humate is generally able to maintain Au in solution. Major exceptions are:

- (i) humate 1 mixtures with Au concentrations greater than 10 mg/L (based on results from Experiment A; Section 3.2.2);
- (ii) humate 2 mixtures, which have lowered levels of Au in the $<0.45 \mu\text{m}$ fraction;
- (iii) dilute (2.5 mg/L OC) humate 3 mixtures.

These results may indicate why there is such diverging opinions on the effect of soluble organic matter on Au (Section 1). Different organic materials may either maintain Au in solution, or precipitate Au. Controlling factors could include concentration of humate, concentration of Au, and the source of the organic matter.

3.3.3. Spectrophotometry of the Experiment B Solutions

As described in Section 3.2.3, spectrophotometry of a number of the solutions indicated the presence of a regular absorption peak around 530 nm. Spectrophotometric analysis was conducted to observe whether this peak was observed for mixtures of each of the three different organic solutions used, and across a wide range of Au:humate ratios.

The spectra of 6.4 mg/L humate 1 / 10 mg/L Au is shown in Fig. 16.

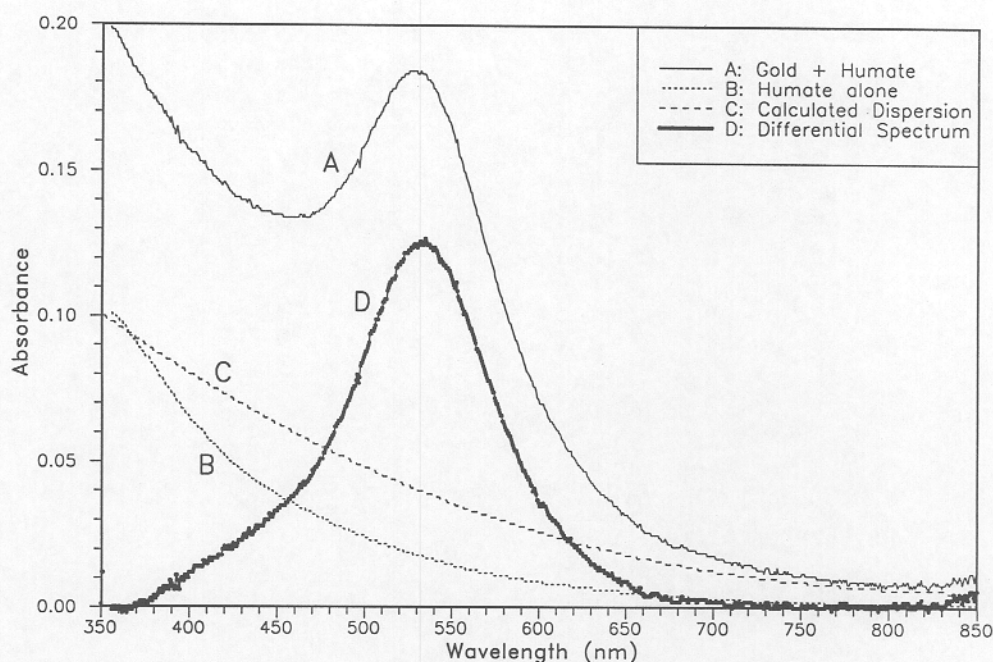


Figure 16: Illustration of the Components used for Differential Spectral Analyses. The Example is of a Solution containing 10 mg/L Au and 6.4 mg/L Humate 1.

The uppermost spectrum in Fig. 16 (curve A) represents the spectrum of a solution containing 10 mg/L Au and 6.4 mg/L humate 1. This absorption pattern can be conceptualized to be the sum of three separate patterns:

- (i) light absorption by Humate 1 alone (curve B);
- (ii) a light dispersion effect, possibly due to aggregation of the Au and/or humate molecules to larger (though still sub-micron) aggregates (curve C);
- (iii) a light absorption by the particular Au-humate species (curve D).

The light absorption of humate can be easily determined by running the spectrum of humate alone, as shown as pattern B in Fig. 16. When this is subtracted from pattern A, there is still an additional background (pattern C), suspected to be due to light dispersion from molecular aggregation. As discussed in Section 4, this background is observed as part of a standard Au sol spectrum. As curves B and C are similar (both decreasing smoothly with increasing wavelength), it is therefore very difficult to resolve curve C when the humate concentration is high and curve B is therefore increased in intensity by up to two orders of magnitude. For this reason, curve C has been "factored out" in these experiments, so as to allow direct comparison between all solutions. This was done by calculating a standard background, so as to bring the background for the final corrected spectrum (*i.e.*, the calculated absorbance at 350 nm or 750 nm) to near zero, giving the final corrected spectrum shown as curve D in Fig. 16. A sample with a high light dispersion, and a low humate concentration was used in this example, for clarity.

Other solutions have much higher humate: Au ratios and the 530 nm absorption peak, if present, will be swamped by the background absorption of the humate. Under these circumstances, the absorption peaks can only be resolved by subtracting the absorption due to humate, as described above. Such subtractions were done on digital absorbance data and results are shown in Figs. 17 - 26.

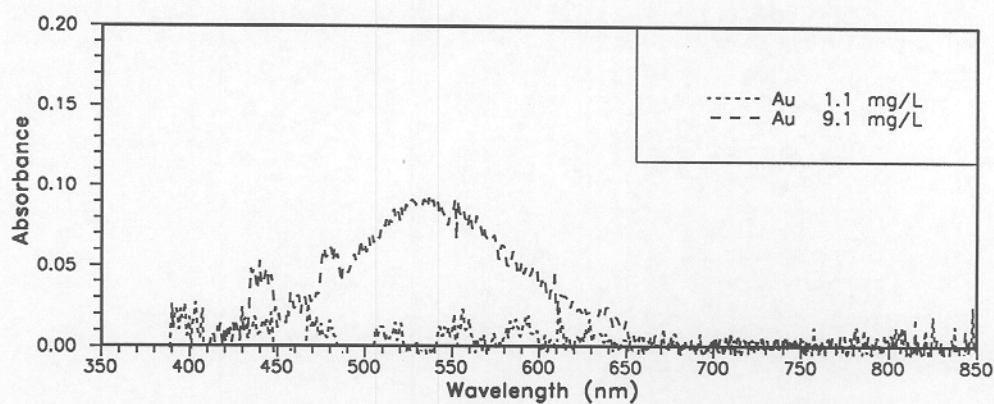


Figure 17: Corrected Spectra of 640 mg/L Humate 1 / Au solutions, with Au concentrations given in the key.

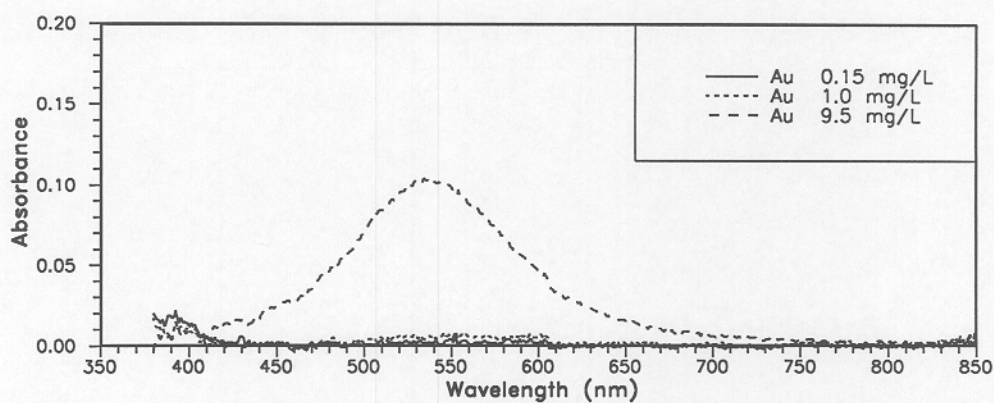


Figure 18: Corrected Spectra of 64 mg/L Humate 1 / Au solutions, with Au concentrations given in the key.

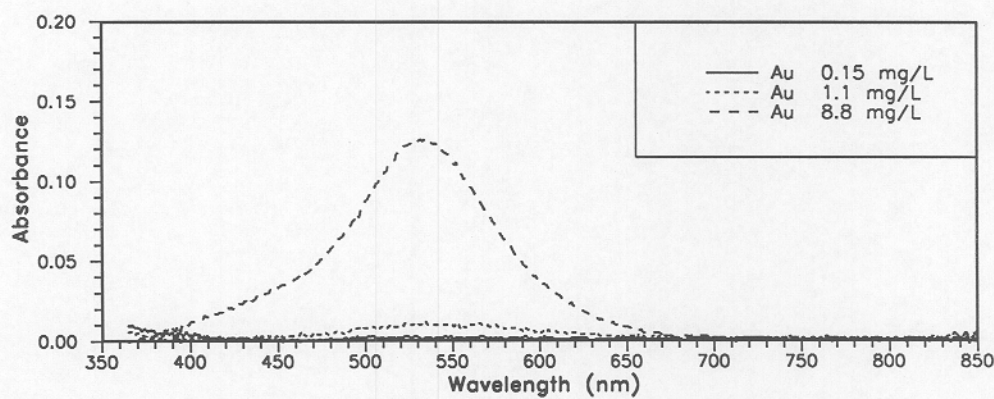


Figure 19: Corrected Spectra of 6.4 mg/L Humate 1 / Au solutions, with Au concentrations given in the key.

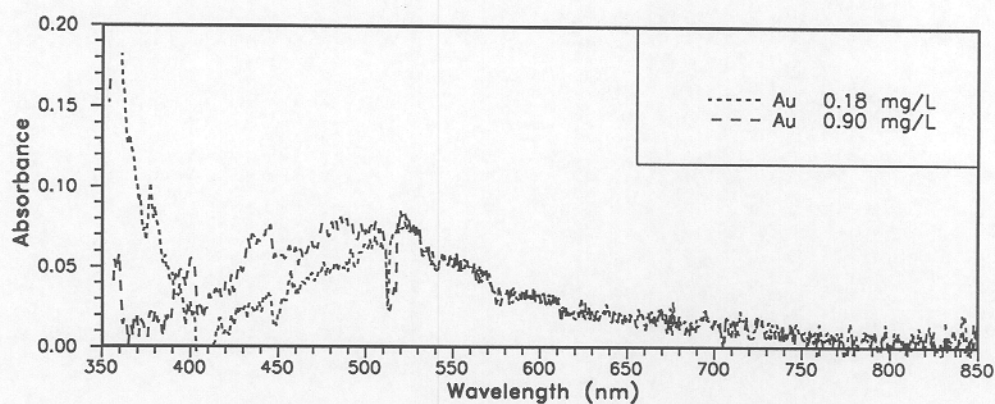


Figure 20: Corrected Spectra of 1300 mg/L Humate 2 / Au solutions, with Au concentrations given in the key.

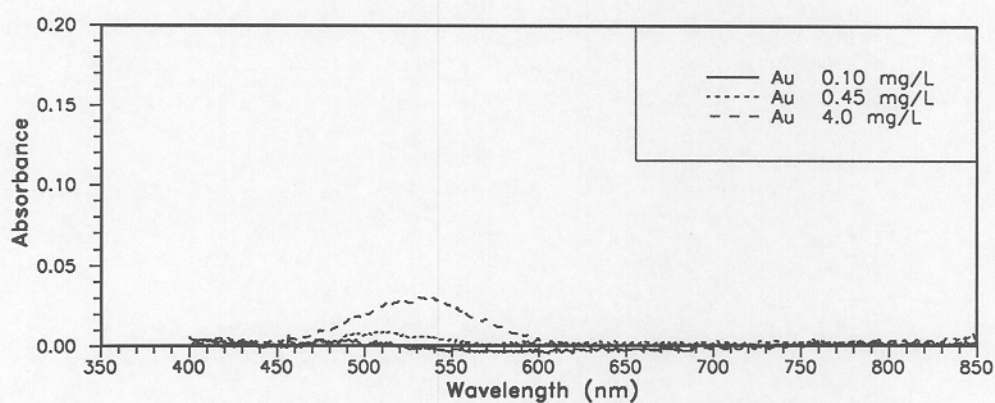


Figure 21: Corrected Spectra of 130 mg/L Humate 2 / Au solutions, with Au concentrations given in the key.

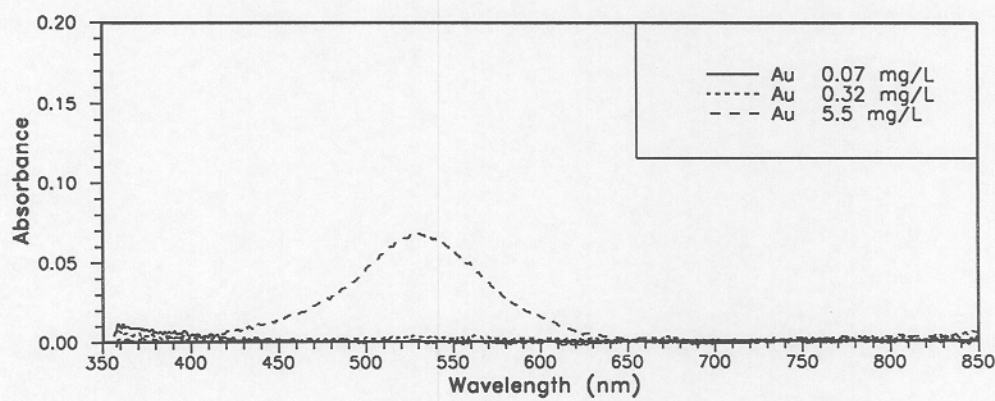


Figure 22: Corrected Spectra of 13 mg/L Humate 2 / Au solutions, with Au concentrations given in the key.

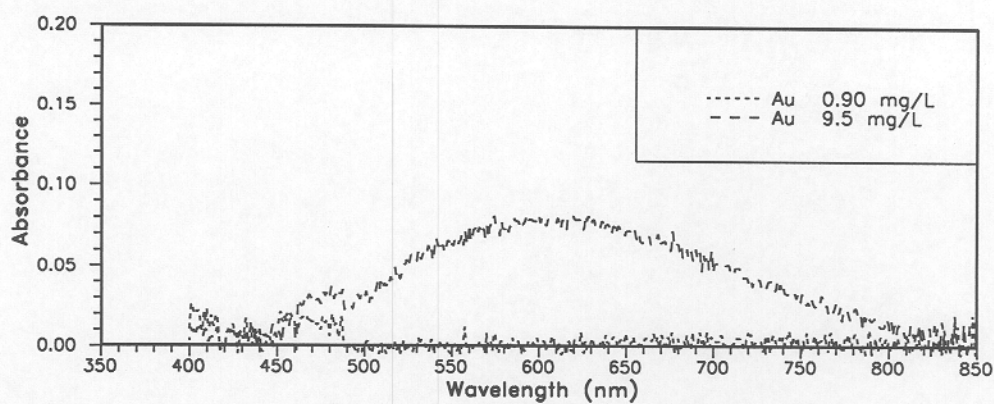


Figure 23: Corrected Spectra of 250 mg/L Humate 3 / Au solutions, with Au concentrations given in the key.

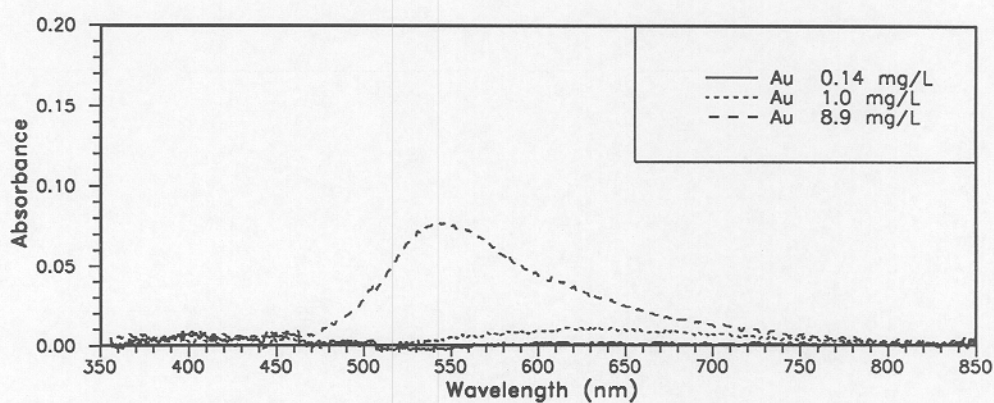


Figure 24: Corrected Spectra of 25 mg/L Humate 3 / Au solutions, with Au concentrations given in the key.

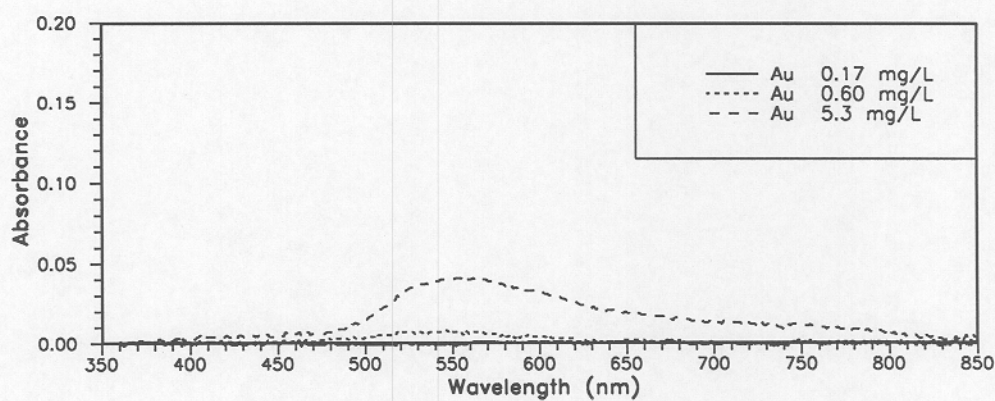


Figure 25: Corrected Spectra of 2.5 mg/L Humate 3 / Au solutions, with Au concentrations given in the key.

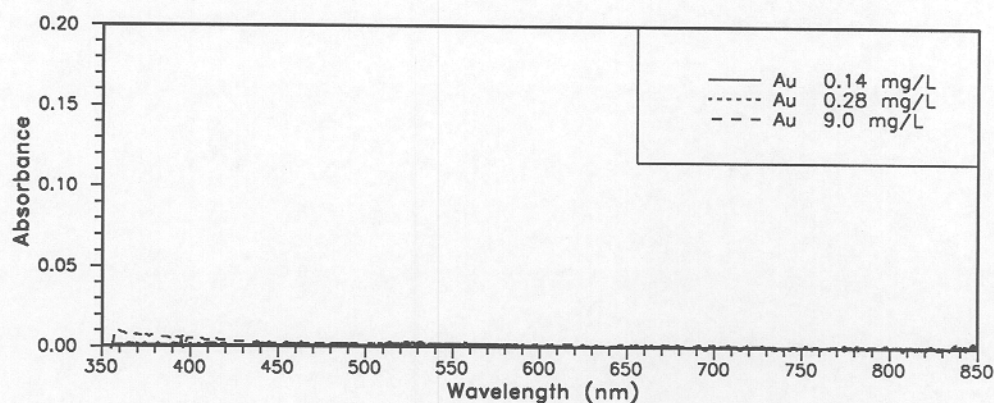


Figure 26: Spectra of Au chloride solutions, with Au concentrations given in the key.

The spectra of samples with a high humate content have a poorer signal to noise ratio than those with low humate contents because the resolved curve is the difference between two large absorbances. Never the less, the shape and position of the absorption peak remains constant, particularly for solutions containing humate 1 (Figs. 17 - 19) and humate 2 (Figs. 20 - 22). Solutions containing humate 3 (Figs. 23 and 24) differ in that the absorption peak appears to be broader and at a higher wavelength at lower Au/humate ratios. At higher Au/humate ratios (Figs. 24 and 25), this effect is less and the absorption peak is similar to that of humate 1 and humate 2 solutions, though it is broadened towards higher wavelengths.

In general, only solutions with the higher concentrations of Au have a 530 nm absorption peak that could be resolved from background. However, in some of the samples with low humate content (Figs. 19, 24 and 25), the peak could be resolved for solutions having Au concentrations of approximately 1 mg/L. The lack of peak resolution is due to the low signal to noise ratios for the low Au samples. It is, of course, possible that these solutions also have the 530 nm absorbance peak, but it cannot be determined under the experimental conditions used.

The peak height of the 530 nm absorption peak is clearly correlated with the concentration of Au in the $<0.45 \mu\text{m}$ fraction of each solution, as shown in each figure and illustrated in Fig. 27. There is a very good linear correlation between absorbance and concentration, with the line of best fit effectively going through the origin. The constant peak position, shape and absorbance/concentration ratio indicates that the Au is present as a species with a specific chemistry. The change in the peak shape and peak position for the humate 3 solutions with high humate:Au ratios (Figs. 23 and 24), however, suggests that the specific chemistry of the Au is changed under these conditions.

The slope of the line of best fit can be used to calculate the molar absorptivity (E_{max} ; measured in $\text{M}^{-1} \cdot \text{cm}^{-1}$), which is a measure of the absorbance per mole per cm of light path. The calculated E_{max} of the Au-humate species was $2200 \text{ M}^{-1} \cdot \text{cm}^{-1}$. The relevance of this measurement is discussed in Section 4.2.

In summary, spectrophotometry of the Experiment B solutions indicates that the interaction of Au with the three soluble organic materials resulted in a highly coloured Au sol. Using differential spectral analysis, the Au sol "colour" was observed even in humate-rich solutions. The light absorption characteristics of this sol was remarkably constant (Fig. 17 - 25) for differing organic phases, differing organic concentrations (from 2.5 to 640 mg/L OC) and differing Au concentrations (1 - 10 mg/L), suggesting that the Au is present as a species with a

specific chemistry. The humate 3 samples (Figs. 23 - 25) differed in that the absorption peak appeared to be broadened and shifted to higher wavelength (> 600 nm) at higher organic: Au ratios.

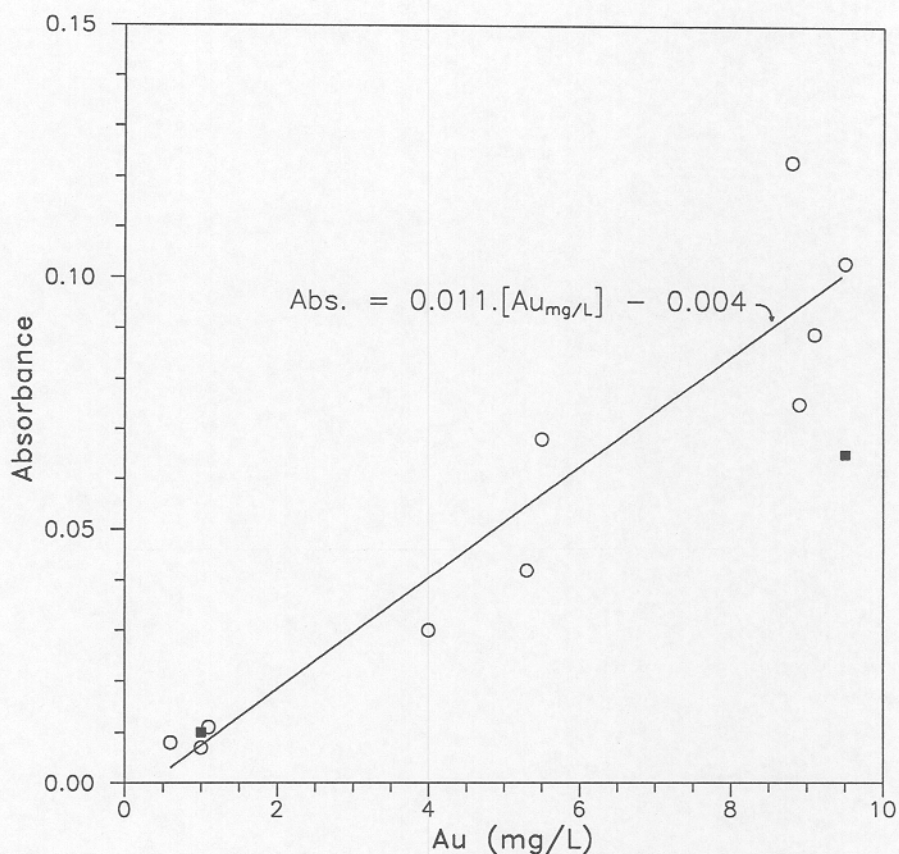


Figure 27: Absorbance of the 530 nm Peak vs. Au concentration for Experiment B solutions. Solid squares indicate the peak heights of the broad, shifted peaks observed for the solutions with high concentrations of humate 3 (*i.e.*, Fig. 23 - 9.5 mg/L Au and Fig. 24 - 1.0 mg/L Au).

3.4. Experiment C

3.4.1. Methods

After 50 days equilibration, the suspensions from Experiment A (Section 3.2) were shaken with various solutions, at a 1:1 ratio, and the spectrum of the solution recorded at 30 min., 2 hr., 20 hr and 3 days. The solutions were:

- (i) deionized water;
- (ii) 0.02 M NaCl;
- (iii) 0.2 M NaCl;
- (iv) 2 M NaCl;
- (v) 0.002 M HCl;
- (vi) 2 M HCl;
- (vii) 1 M H₂SO₄

- (viii) 0.002 M NaOH;
- (ix) 2 M NaOH;
- (x) 0.04 M cyanide (CN^-);
- (xi) 0.1 M iodide (I^-);
- (xii) 0.1 M thiosulphate ($\text{S}_2\text{O}_3^{2-}$);
- (xiii) 0.1 M thiocyanate (SCN^-);
- (xiv) 0.0002 M ascorbic acid (Asc);
- (xv) 0.02 M Asc;
- (xvi) 0.2 M Asc;

These solutions were chosen so as to include a range of ligands (*i.e.*, Cl^- , OH^- , CN^- , $\text{S}_2\text{O}_3^{2-}$ and SCN^-) that could tend to complex the Au, and therefore convert it back to ionic form. In addition, acid and base solutions, and ascorbic acid were also used to test the stability of the Au sol.

Additional treatments were used to test whether removal of oxygen affected the conversion of Au sol to ionic complexed Au, or whether concentrated ascorbic acid affected the stability of the sol:

- (i) separate solutions of 100light, 100dark, 10light and 10dark were all deoxygenated by N_2 bubbling for at least 20 min. Following this a deoxygenated solution of 2% potassium cyanide (KCN) / saturated calcium oxide (CaO) was added to the four solutions at a 1:1 ratio, and the colour change monitored at 2 and 20 min.
- (ii) separate solutions of 10light and 10dark were deoxygenated by N_2 bubbling for at least 20 min. Following this a deoxygenated solution of 0.1 M I^- was added to the two solutions at a 1:1 ratio, and the colour change monitored at 2, 20 and 60 min.
- (iii) solid ascorbic acid was added to a solution of 10light, and the colour change monitored.

3.4.2. Results

Results from shaking the suspensions from Experiment A with various solutions are given in Table 3. The colours given were those observed at 30 min., 2 hr., 20 hr and 3 days.

As noted in Table 3, addition of 0.002 M NaOH to solution 100light causes a deep pink solution. Three repeats of this test indicated that the intensity of the colour was dependant on the amount of black solid (normally precipitated from solution 100light; Section 3.2.2) shaken with the NaOH solution. Thus, if solution 100light was allowed to settle for several days and the aliquot taken from the top of the container, mixing with 0.002 M NaOH did not show any colour change. If a well-mixed slurry of solution 100light was shaken, or the aliquot taken from the bottom of the container, mixing with 0.002 M NaOH gave a pink solution. After filtering through a $<0.45 \mu\text{m}$ membrane filter, the pink solution showed the standard Au sol spectrum (Fig. 28).

Table 3: Reactions of Experiment A Suspensions with Various Solutions.

Solution	Colour change observed for suspension at 30 min., 2 hr., 20 hr and 3 days.			
	100light	100dark	10light	10dark
deion. water	Br → Br → Br → Br	Yl → Yl → Yl → Yl	Pk → Pk → Pk → Pk	Pk → Pk → Pk → lPk
0.02 <u>M</u> NaCl	nd	nd	Pk → Pk → Pk → Pk	nd
0.2 <u>M</u> NaCl	nd	nd	lPk → vlPk → vlPk → Cl	nd
2 <u>M</u> NaCl	nd	nd	Cl → Cl → Cl → Cl	nd
0.002 <u>M</u> HCl	Br → Br → Br → Br	Yl → Yl → Yl → Yl	Pk → Pk → Pk → Pk	Pk → Pk → Pk → Pk
2 <u>M</u> HCl	Br → lBr → lBr → lBr	Yl → Yl → Yl → Yl	lPk → lPk → lPk → lPk	lPk → vlPk → lPk → vlPk
1 <u>M</u> H ₂ SO ₄	nd	nd	lPk → lPk → lPk → vlPk	nd
0.002 <u>M</u> NaOH	Pk → Pk → dPk → dPk [#]	Yl → Yl → Yl → Yl	Pk → Pk → Pk → lPk	Pk → Pk → Pk → Pk
2 <u>M</u> NaOH	Yl → Yl → Yl → Yl	Yl → Yl → Yl → Yl	Cl → Cl → Cl → Cl	Cl → Cl → Cl → Cl
0.04 <u>M</u> CN ⁻	*Yl → Yl → Yl → Yl	Yl → Yl → Yl → Yl	Cl → Cl → Cl → Cl	Cl → Cl → Cl → Cl
0.1 <u>M</u> I ⁻	Br → Br → Br → Br	Yl → Yl → Yl → Yl	lPk → lPk → vlPk → Cl	lPk → lPk → lPk → Cl
0.1 <u>M</u> S ₂ O ₃ ²⁻	Br → Br → Br → Br	Yl → Yl → Yl → Yl	lPk → Cl → vlPk → Cl	Pk → lPk → lPk → lPk
0.1 <u>M</u> SCN ⁻	Br → Br → Br → Br	Yl → Yl → Yl → Yl	lPk → lPk → lPk → vlPk	Pk → lPk → lPk → lPk
0.0002 <u>M</u> Asc	Br → Br → Br → Br	Yl → Yl → Yl → Yl	Pk → Pk → Pk → Pk	Pk → Pk → Pk → Pk
0.02 <u>M</u> Asc	Br → Br → Br → Br	Yl → Yl → Yl → Yl	Pk → Pk → Pk → Pk	Pk → Pk → Pk → Pk
0.2 <u>M</u> Asc	Br → Br → Br → Br	Yl → Yl → Yl → Yl	Pk → Pk → Pk → Pk	Pk → Pk → Pk → lPk

* Immediate red change then yellow

Repeated three times. See below for further details.

Br: brown

lBr: light brown

Yl: yellow

Pk: pink

lPk: light pink

vlPk: very light pink

dPk: deep pink

Cl: clear

nd: not determined

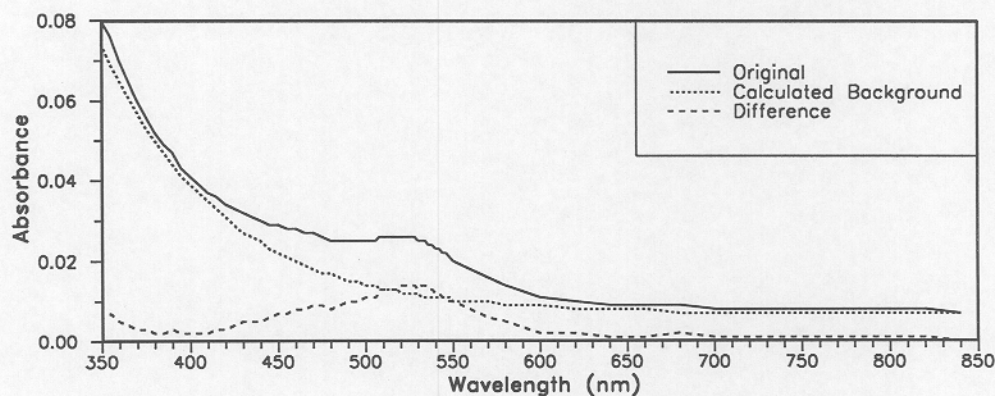


Figure 28: Corrected Spectra of Solution 100light + 0.002 NaOH.

Results from addition of N₂-bubbled solutions of 2 % KCN and of 0.1 M KI to N₂-bubbled Au humate suspensions, as well as from addition of solid ascorbic acid to a solution of 10light, are given in Table 4.

Table 4: Results from Addition of KCN and KI (with N₂ bubbling), and of solid Ascorbic Acid, to Experiment A Suspensions.

Solution	Colour change observed for suspension before addition, at 2 min., 20 min., and at 60 min.			
	100light	100dark	10light	10dark
2% KCN (with N ₂ bubbling)	Br → lBr → lBr	Yl → lYl → lYl	Pk → lPk → Cl	Pk → lPk → Cl
0.1 M KI (with N ₂ bubbling)	nd	nd	Pk → lPk → vlPk → Cl	Pk → lPk → vlPk → Cl
Solid Ascorbic Acid	nd	nd	Blue Precipitate	nd

Br: brown

lBr: light brown

Yl: yellow

lYl: light yellow

Pk: pink

lPk: light pink

vlPk: very light pink

Cl: clear

nd: not determined

The results summarized in Table 3, show that a number of the ligands decolourize the 10light and 10dark suspensions. This is probably due to the break-up of the humate species and formation of a new complex. Differing ligands decolourize the suspensions at different rates. The order observed was $\text{CN}^- > \text{I}^- > \text{S}_2\text{O}_3^{3-} > \text{SCN}^- > \text{Cl}^-$, which is roughly similar to the order of the strength of bonding with Au^+ (*i.e.*, $\text{CN}^- > \text{S}_2\text{O}_3^{3-} > \text{SCN}^- > \text{I}^- > \text{Cl}^-$)³. The principal difference is that I^- decolourizes the suspension much more quickly than would be expected from thermodynamic factors alone. The 2 M NaOH solution also decolourizes the 10light and 10dark suspensions, possibly due to complexation of the Au as $\text{Au}(\text{OH})_2^-$, or to decomposition of the active groups in the humate by the alkaline conditions. The characteristic Au sol colour was observed when suspension 100light was shaken with 0.002 M NaOH (Fig. 28), indicating that Au sol had been precipitated under these conditions, and was redissolved by the alkaline treatment. This result was not observed for 100dark, again implying Au sol formation is activated by light.

Shaking of the Au-humate solutions with ascorbic acid solutions showed little reaction (Table 3). This result is consistent with the Au being present as Au^0 , since if Au were present as a weakly complexed cation (Au^+ or Au^{3+}) ascorbic acid would be expected to reduce it. Assuming that Au was present as a neutral sol, then decolourization would be expected to be slow when CN^- or I^- is added and the solutions have been deaerated, as O_2 (or some other electron acceptor) is required to oxidize the Au from Au sol to Au^+ so that it can then be complexed. However, decolourization of the suspensions, following addition of KCN or KI in N₂-bubbled solutions, was fast (Table 4), despite the absence of dissolved O_2 . It is possible that various groups within the soluble organic phase could act as electron acceptors.

If it is accepted that Au is present as Au^0 , then it is difficult to explain the loss of the pink colour and formation of a blue precipitate after mixing with solid ascorbic acid. It is possible that the Au is present as a multi-atom mass (*i.e.*, a metal sol), with a small remaining positive charge, and that adding excess solid ascorbic

³ The thermodynamics of the various Au complexes of importance are discussed in Gray (1988).

acid reduces the Au completely and initiates aggregation and precipitation. However, such a hypothesis is provisional and further work is obviously required.

In summary, results from Experiment C indicate that the Au-humate species is only weak, and Au in the metal sol is converted into ionic form by CN^- , I^- , $\text{S}_2\text{O}_3^{3-}$, SCN^- , and even by concentrated Cl^- . In addition, ascorbic acid additions suggest the Au to be present in a neutral, or near-neutral, form. Determinations of the charge on the Au by this method is complicated by the redox active nature of the humic matter.

3.5. Experiment D

This experiment was conducted to observe whether other metals reacted with humate in a similar manner to Au. Mixtures were prepared by adding a specified amount of a particular metal to a 6.4 mg/L humate 1 solution. The solutions were then taken to pH 7 with either sodium hydroxide (NaOH) or hydrochloric acid (HCl) solution, and stored in glass, with intermittent shaking.

The mixtures used in Experiment D were:

- (i) 10 mg/L Cu / 6.4 mg/L humate 1;
- (ii) 10 mg/L Ag / 6.4 mg/L humate 1;
- (iii) 10 mg/L Pd / 6.4 mg/L humate 1;
- (iv) 10 mg/L Pt / 6.4 mg/L humate 1;

The mixtures were then left for 11 months with intermittent shaking. In all of these cases the resulting solutions were colourless, *i.e.*, there was no visible absorption, as observed for the Au-humate mixture. Therefore, the facile formation of Au sol in the presence of humate bonding does not appear to have an analogous reaction for these other metals.

4. Discussion

4.1. General Observations

Investigation of the chemistry of the interaction of Au with humate is ongoing, and this report represents a summary of work completed to date. In general, the results obtained to date have shown that Au has a highly variable behaviour in humate solution, depending on the concentrations of the reagents. In particular, where the initial concentration of Au is 100 mg/L, addition of soluble organic matter tends to precipitate Au (Section 3.2.2). At lower concentrations (0.1 - 10 mg/L), the size distribution of the Au is dependant on the Au concentration, organic matter concentration and organic matter source (Section 3.3.2). Thus, Au is extremely soluble in the ranges of 0.1 to 10 mg/L when shaken with concentrations of humate 1 between 6.4 and 640 mg/L (Figs. 7 - 9) and with concentrations of humate 3 between 25 and 250 mg/L (Figs 13 and 14). However, Au concentrations in the $<0.45 \mu\text{m}$ fraction are markedly decreased for the humate 2 suspensions (Figs 10 - 12), particularly at high organic matter concentrations ($>1000 \text{ mg/L}$; Fig. 10), and also for lower concentrations of humate 2 (2.5 mg/L; Fig. 15). Results for the humate 2 suspensions indicate that there are phases within the humate 2 which tend to precipitate Au, via mechanisms as yet not determined. The poor solubilities of Au in 2.5 mg/L humate 3 may indicate that Au is not soluble at lower levels of humate. This correlates with the observations of Ong and Swanson (1969), that Au was soluble in the presence of 30 mg/L organic acid, but precipitated when only 3 mg/L organic acid was present.

The high variability in Au solubility possibly explains the large disparities in the literature (Frieze, 1931; Fetzer, 1934, 1946; Ong and Swanson, 1969; Baker, 1973, 1978; Boyle *et al.*, 1975; Fedoseyeva *et al.*, 1986). Never the less, it is not clear why Au humate is stable at Au concentrations of 10 mg/L, but not 100 mg/L, nor why humate 2 does not stabilize Au in the $<0.45 \mu\text{m}$ fraction as effectively as humates 1 and 3. A deeper understanding of both the chemistry of the humate material itself and of the interaction of humate with Au is clearly required in order to understand this potentially important mechanism for Au dissolution and precipitation in natural systems.

The work of Ong and Swanson (1969) clearly indicated that, under their experimental conditions, the interaction of Au with organic acids has resulted in the presence of highly coloured Au sols ($<10 \text{ nm}$), stabilized by fine (2.4 - 10 nm) hydrophilic organic acids. Subsequent experiments by Fedoseyeva *et al.* (1986) demonstrated that Au sols could be stabilized in the presence of humic and fulvic acids. In addition, these workers measured the spectra of the sols and tried to form the sols by interacting humic and fulvic acids with different Au complexes (rather than just with AuCl_2^- , as in Ong and Swanson, 1969).

The data from the present study has generally confirmed the conclusions of Ong and Swanson (1969) and Fedoseyeva *et al.* (1986). General conclusions are detailed below:

(i) The formation of stabilized Au sols via the interaction of soluble humic matter with ionic Au appears to be a general phenomenon. The spectrophotometric data (Section 3.3.3) indicate this to occur even when the organic matter is in major excess. Unfortunately, this method is not sensitive enough to test for the presence of Au sol where the Au concentration is below 1 mg/L.

(ii) There is some evidence that the formation of the Au sol is activated by light. Comparison of the Au size distribution in, and the spectra of, solution 100light compared with solution 100dark, and solution 10light compared with solution 10dark (Section 3.2) indicated Au to be more soluble, and the Au sol spectra to be more generally observed, when the solutions were exposed to the light. Addition of dilute base to aged solution 100light (Section 3.4.2) gave the characteristic Au sol colour (Fig. 28), indicating that Au sol had been formed and then precipitated. No such result was observed for solution 100dark. These results are consistent with the observations of Fabrikanos *et al.* (1963), who found that the formation of Au sols could be activated by ultra-violet (UV) light. Note, however, that Au sol formation can occur even in the absence of light (*e.g.*, solution 10dark; Fig. 6), presumably where its formation is strongly preferred. This light activation effect is expected to be more important for surface waters, such as streams and lakes, than subsurface solutions.

(iii) The phenomenon of Au sol formation was observed not only for a purified humate such as humate 1, but also for humates 2 and 3. These humates were generated by immersing leaves and twigs in water for 12 months, with no attempt to separate large molecular weight organic phases from non-humic compounds (Sections 1 and 2). Thus, with the materials and experimental conditions used here, compounds such as CN^- , sulphur-containing amino acids or amine-rich molecules were not produced in sufficient quantities to interfere with the formation of Au sol, at the Au concentrations tested: *i.e.*, Au sol formation dominated over ionic Au complexation in the simulated organic-rich soil solutions. However, it would be extremely valuable to develop methods to test this hypothesis at lower Au concentrations (1 - 100 $\mu\text{g/L}$), which would be expected to be more representative of natural solutions.

(iv) Fedoseyeva *et al.* (1986) attempted to form Au sol by mixing humic or fulvic acid with various Au complexes. They found that Au sol was readily formed when the starting Au complexes were the weak and easily reduced Cl^- and Br^- complexes. The stronger complexes AuI_2^- , $\text{Au}(\text{SCN})_4^-$, $\text{Au}(\text{SO}_3)_2^{3-}$, $\text{Au}(\text{S}_2\text{O}_3)_2^{3-}$ and $\text{Au}[\text{SC}(\text{NH}_2)_2]^{2+}$ were not reduced by the humic or fulvic acids. Similarly Fabrikanos *et al.* (1963) found that ethylenediaminetetraacetic acid (EDTA) could reduce AuCl_4^- , but not AuI_2^- . Thus, the formation of Au sol will be limited where major quantities of Au ligands such as I^- or $\text{S}_2\text{O}_3^{2-}$ are present. Experiment C (Section 3.4) tested the extent to which various ligands could disrupt existing Au sol humate species. Results (Section 3.4.2; Table 3) indicate that ligands with a weak affinity for Au (*e.g.*, Cl^-) will decolourize the solutions only when present at high concentrations, whereas ligands with moderate affinity for Au (*e.g.*, I^- , $\text{S}_2\text{O}_3^{2-}$, SCN^-) can complex the Au within days, and solutions containing CN^- decolourize the sol within minutes. The formation of Au sol with humates 2 and 3 indicates that these soluble organic mixtures cannot contain high levels of such ligands.

(v) The colour of the Au sol, and in particular the diagnostic absorption peak at about 530 nm (Fig. 16), is highly useful in determining the form of the Au, even where the colour has been obscured by the presence of organic matter. In addition, this peak may indicate important details on the size or chemistry of the Au sol. The constancy of the absorption peak, both in terms of position (Figs. 3, 5, 6, 17 - 22, 24 and 25) and intensity (Fig. 27) is especially significant. In the few instances where the position of the peak does vary (Figs. 23 and 24), it does so dramatically, rather than showing any gradual differences. Almost identical spectra, including the "dispersion" background (Section 3.3.3: Fig. 16), were observed by Fedoseyeva *et al.* (1986) for Au sols formed with humic and fulvic acid, and by Fabrikanos *et al.* (1963) for Au sol formed with EDTA. Fabrikanos *et al.* (1963) state that the intense absorption is a particle size effect, and that the peak position can be used to calculate a particle size of 20 nm diameter, based on the theory of Mies (1908), though no explanation of the method used is

given. The theory of Mies is highly complex, and it is not clear to the authors at this point how this calculation is performed. However, future work on this topic will include testing this calculation.

A particle size of 20 nm diameter is certainly within the range expected, though the Au sols formed by Ong and Swanson (1969) were found to pass through a 10 nm membrane filter, contradicting this calculation. The constant peak position indicates that if the theory were correct, the particle size of the Au sol would be the same in all cases. However, studies on the particle sizes of Au sols formed by citrate and hydroxylamine reduction (Turkevich *et al.* 1953; Frens, 1972) indicate major variation in the particle size of the synthesized Au sol, depending on reagent conditions. Frens (1972) found particle size to be varied between 8 and 70 nm, with a major factor in the variation being citrate concentration. It therefore seems highly unlikely that solutions containing differing organic compounds, from humic acid to dissolved leaf material to EDTA, at widely varying concentrations of Au and organic material, should all produce sols of virtually identical particle size. This hypothesis can be further tested by electron microprobe analyses of the Au sol, and such studies will be initiated as an extension of this work.

4.2. Chemical Significance of the 530 nm Absorption Peak

If the intense visible absorption is not a particle size effect, then what is its cause? The results suggest that the absorption is due to an effect that is constant for a variety of Au sols. From this, it can be inferred that the absorption is 'chemical' rather 'physical' and is therefore conceptually similar to standard light absorptions by other soluble compounds.

The peak position and molar absorptivity (E_{max} ; Section 3.3.3) of the Au-humate sol, and a variety of other complexes are compiled in Table 5. All elements and compounds show strong light absorption in the UV region (< 350 nm). These light absorptions represent photons of particular energy being absorbed, resulting in the transition of an electron from its normal energy level to a higher energy molecular orbital (Fig. 29). Because the differences in molecular orbital energies are fixed, and are a function of the element and its bonding, only photons of a particular energy are adsorbed. As the wavelength of the light is inversely proportional to its energy⁴, then this corresponds to absorption of light of a particular wavelength.

Broad spectral peaks, as observed here (*e.g.*, Fig. 16) are common for ions in solution, due to molecular orbital energy ranges being broadened by vibrational processes. The UV absorption peaks of a few elements and compounds are given in Table 5. These electronic transitions typically have molar absorptivities of 10^3 to 10^5 .

⁴ Specifically the mathematical relationship is:

$$E = \frac{hc}{\lambda}$$

where E = energy of radiation (J)
 h = Planck's constant ($= 6.63 \times 10^{-34}$ J s)
 c = speed of light (3.0×10^8 m/s)
 λ = wavelength (m)

Table 5: Peak Position and E_{\max} of the Au-humate Species and a Variety of other Complexes.

Compound	Peak Position (nm)	E_{\max}	Source
NO_3^-	302	710	4
AuCl_4^-	225	68000	3
	313	11000	
Cu^{2+}	275	3400	3
	385	5700	
Fe^{3+}	225	7000	3
	320	2900	
	360	3100	
$\text{Cr}_2\text{O}_7^{2-}$	257	4300	4
	350	3200	
$\text{Fe}(\text{CN})_6^{3-}$	260	1200	2
	300	1700	
	420	1000	
MnBr_4^{2-}	360	3.8	2
$\text{Co}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_3^{3+}$	350	82	2
	470	78	
$\text{Ti}(\text{H}_2\text{O})_6^{3+}$	500	5	2
$\text{Cr}(\text{H}_2\text{O})_6^{3+}$	407	16	5
	574	13	
MnO_4^-	311	1700	6
	507	1780	
	523	2390	
	545	2310	
Au-humate	530	2200	1

- 1: This report.
- 2: Cotton and Wilkinson (1980).
- 3: Goodkin *et al.* (1975).
- 4: Calculated from Edisbury (1966).
- 5: Gray (1982).
- 6: Unpublished work by D.J. Gray.

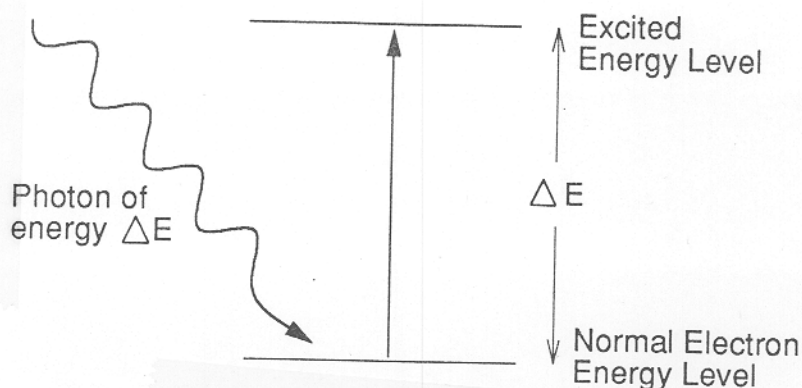
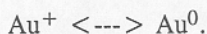


Figure 29: Mechanism of Light Absorption.

Only a small proportion of compounds have measurable absorption peaks in the visible region. This is because visible photons have a higher wavelength, and therefore a lower energy. In most compounds, the molecular energy differences are greater than the visible photon energies and the photons do not interact with the compound. The net result is that the compound is transparent to visible light. Exceptions to this occur when the molecular orbital energy differences are smaller than normal, such as in transition metal complexes. In these complexes the energies of the d orbitals, which all have the same energy in the elemental state, are slightly split by the electronic influence of the ligands. The resulting energy difference corresponds to the visible region of the spectrum and results in coloured solutions. Examples of such absorbing ions, given in Table 3, are MnBr_4^{2-} , $\text{Co}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_3^{3+}$, $\text{Ti}(\text{H}_2\text{O})_6^{3+}$ and $\text{Cr}(\text{H}_2\text{O})_6^{3+}$. Note, however, that the E_{max} of these metal complexes is very low (< 100), relative to the "normal" UV absorbances. This is because the transitions are between molecular orbitals of the same symmetry (that were once of the same energy) and the transitions are not allowed according to classic theory.

Intense visible absorptions occur from two major sources. The first is carbon compounds with conjugated double bonds. This effect is discussed in major detail in various texts (*e.g.*, Streitwieser and Heathcock, 1976, pp 529-605). However, it will not be the mechanism for the intense light absorption by Au sol, as this occurs even in the absence of carbon (Fabrikanos *et al.*, 1963). The second major source of intense visible light absorption is charge transfer transitions, in which the electron moves from a molecular orbital centered mainly on the ligands to one centered mainly on the metal ion, or *vice versa*. An example of this is for permanganate, in which the charge transfer would be between the ligand oxygen and the highly oxidised Mn ion (Cotton and Wilkinson, 1980). One explanation for the colour of the Au sol is that the absorption is a charge transfer peak, with the Au ion jumping between different oxidation states:



Alternatively the electronic transition could be between molecular orbitals that are formed in the bonding of the Au to form a sol, which may well be different from a "normal" compound. If the light absorption peak at 530 nm is due to either of these effects, the spectra are giving information on the type of bonding, rather than, as previously expected, on the particle size of the Au.

Any future work on the interaction of Au with humate material (either soluble or insoluble) should involve determining the nature of this bond.

5. Summary

Soluble humic material from various sources was found to readily reduce Au chloride to a Au sol. This sol was stabilized in solution, presumably by the presence of humate. The amount of Au stabilized in solution was dependant on a number of factors, including type of humate, concentration of humate, concentration of Au, and presence or absence of light. This reaction did not occur for Ag, Cu, Pt or Pd, under the conditions of the experiment.

Shaking Au sol with various ligand solutions indicated that the sol was readily oxidized and complexed by ligands with strong (CN^-) or moderate (I^- , $\text{S}_2\text{O}_3^{2-}$, SCN^-) affinities for Au, or by ligands with weak (Cl^-) affinities for Au when in high concentration.

Spectral analysis described in this report, and elsewhere, indicates the Au sol to have a highly constant light absorption pattern. Therefore either the sol has a very constant size, or the absorption is due to other chemical factors, and may therefore represent a source of information on the chemistry of the Au in these conditions.

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