Chromatographic and Electromigrative Determination of Sulfur-Oxygen Anions in Gold Thiosulfate Leach Solutions

by

John William O'Reilly

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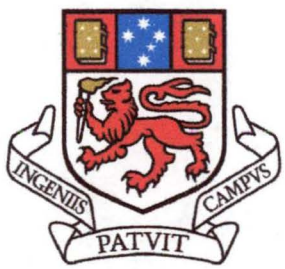

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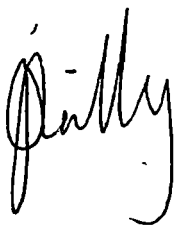

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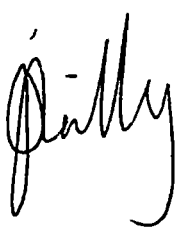

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DEDICATION

I would like to dedicate this thesis to the memory of my late grandmother,

Isobel Amelia O'Reilly

to whom seeing the completion of this work would have meant so much.

LIST OF ABBREVIATIONS

2-PrOH	2-Propanol
Ac	Acetate
ACN	Acetonitrile
BGE	Background electrolyte
Bis-tris	2,2-bis(hydroxymethyl)-2,2',2''-nitrotriethanol
BTC	Benzenetricarboxylate
CE	Capillary electrophoresis
CHES	2-(N-cyclohexylamino)ethanesulfonic acid
CTA	Cetyltrimethylammonium
DEtA	Diethanolamino
DETA	Diethylenetriamine
DTNP	2-2'-dithiobis(5-nitropyridine)
DVB	Divinylbenzene
EDA	Ethylenediamine
EDTA	Ethylenediaminetetraaceitc acid
EtOH	Ethanol
FIA	Flow injection analysis
FTIR	Fourier transform infra-red
GC	Gas chromatography
HAH	Hydroxylamine hydrochloride
HDB	Hexadimethrine bromide
HEMA	Hydroxyethyl methacrylate
HMB	Hexamethonium bromide
HPLC	High performance liquid chromatography
HPMC	Hydroxypropylmethylcellulose

LIST OF ABBREVIATIONS (CONTINUED)

IC	Ion chromatography
ICP-MS	Inductively coupled plasma-Mass spectrometry
IIR	Ion-interaction reagent
ITP	Isotachophoresis
MBB	Monobromobimane
MDEA	methyl-diethanolamine
MeOH	Methanol
min	Minutes
n-BuOH	N-butanol
NS	Not specified
NTS	Naphthalenetrisulfonate
ODS	Octadecylsilica
PAR	4-(2-pyridylazo)resorcinol monosodium salt hydrate
PCR	Post column reaction
PMA	Pyromellitic acid
PrOH	Propanol
RSD	Relative standard deviation
TBA	Tetrabutylammonium
THAM	Tris(hydroxymethyl)aminomethane
THF	Tetrahydrofuran
TPA	Tetrapropylammonium
TrEA	Triethanolamine
Tris	Tris(hydroxymethyl)aminomethane
TTA	Tetradecyltrimethylammonium

LIST OF PUBLICATIONS

Type of Publication	Number	Reference
Papers in refereed journals	4	1-4
Posters at international meetings	2	5-6

1. O'Reilly J. W., Dicinoski G. W., Shaw M. J., Haddad P.R. "Chromatographic and electrophoretic separation of inorganic sulfur and sulfur-oxygen species", *Anal. Chim. Acta* 2001 (432) 165-192
   (Chapter 1)

2. O'Reilly J. W., Shaw M. J., Dicinoski G.W., Grosse A. C., Miura Y., Haddad P. R., "Separation of polythionates and the gold thiosulfate complex in gold thiosulfate leach solutions by ion-interaction chromatography", *Analyst* 2002 (127) 906-911
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3. O'Reilly J. W., "Application of ion-chromatography to gold thiosulfate leach solutions", *Aust. J. Chem.* 2002 (55) 546
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4. O'Reilly, J. W., Dicinoski, G. W., Miura, Y., Haddad, P. R., "Separation of thiosulfate, polythionates and the gold thiosulfate complex in gold thiosulfate leach solutions by capillary electrophoresis", *Electrophoresis*, accepted for publication (2003).
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5. O'Reilly J. W., Dicinoski G. W., Shaw M. J., Haddad P.R., "Determination of gold thiosulfate and polythionates by ion-chromatography", *International Ion Chromatography Symposium IICS'01*, Chicago, USA, 9-12 September 2001.

6. O'Reilly J. W., Shaw M. J., Dicinoski G.W., Miura Y., Haddad P. R., "Determination of gold thiosulfate and polythionates in gold thiosulfate leach solutions by ion-interaction chromatography", *INTERACT 2002,* University of Technology, Sydney, Australia, 21-25 July 2002.

ABSTRACT

This work presents a series of investigations into the use of chromatographic and electromigrative techniques for the analysis of gold thiosulfate leach solutions. The focus of the project was determination of the gold thiosulfate complex ($Au(S_2O_3)_2^{3-}$), thiosulfate ($S_2O_3^{2-}$) , the polythionates ($S_xO_6^{2-}$, x = 3 to 5) and sulfate (SO_4^{2-}) in these liquors.

The fundamental behaviour of the gold thiosulfate complex was studied in an ion-interaction chromatographic system. Partial dissociation or decomposition of the gold complex occurred on-column in standards, although this was minimised through adding thiosulfate to the eluent. Addition of the matrix ions, thiosulfate, trithionate, tetrathionate or the leach matrix to gold thiosulfate samples further complicated the chromatography, with the gold peak area dependent on the concentrations of these species in solution. Broadening of the gold peak occurred in solutions containing high concentrations of thiosulfate or the leach matrix that was in part attributed to a self-elution effect. Other mechanisms were also thought to affect the chromatography, such as the type of stationary phase. These problems prevented the successful determination of gold thiosulfate in the leach matrix.

Ion-interaction chromatography was successfully applied to the determination of trithionate, tetrathionate, and pentathionate in undiluted leach liquors. A total analysis time of 18 min was required for the developed method using a Dionex NS1-5μ column with guard and an eluent comprising an acetonitrile step gradient at injection from 15% to 28% *v/v*, 3 mM tetrabutylammonium hydroxide and 2.5 mM sodium carbonate. Detection limits for polythionates using a 10 μL

injection volume ranged between 5-23 μM for conductivity and 4-68 μM for UV detection based on a signal to noise ratio of 2.

The electromigrative methods, capillary electrophoresis, isotachophoresis and mixed mode isotachophoresis/capillary electrophoresis were also investigated for their applicability to the determination of sulfur-oxygen species in thiosulfate leach liquors. Using capillary electrophoresis a method was developed that allowed the separation of thiosulfate, polythionates and the gold thiosulfate complex. The method separated the five species in under 3 min with a total analysis time of 8 min, using an electrolyte containing 25 mM bis-tris adjusted to pH 6.0 with sulfuric acid and an applied voltage of –30 kV. Quantification of the gold thiosulfate complex was not possible by this technique due to inconsistent peak areas and peak splitting effects induced by the presence of other sulfur-oxygen species in the sample. Detection limits of the method ranged between 0.5-2 μM. The technique was applied successfully to a thiosulfate leach liquor diluted 1:100.

Using isotachophoresis, simultaneous determination of thiosulfate and sulfate, in less than 30 minutes, was possible for a synthetic thiosulfate leach liquor requiring a dilution factor of only 2:5. Detection limits of the developed method were 1.3 mM for sulfate and 2.1 mM for thiosulfate. The method also showed promise for the simultaneous determination of thiosulfate, sulfate, trithionate and tetrathionate in these leach solutions. The concept of single capillary isotachophoresis/capillary electrophoresis for these sulfur ions was also demonstrated, however problems with reproducible quantitation prevented the development of a working method.

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Fundamental Behaviour of the Gold Thiosulfate Complex in an Ion-Chromatographic System

Chapter 1

Literature Review

1.1 Introduction

Gold has been treasured by the human race for millennia, having been valued by some of the earliest known civilisations in Sumeria and Egypt at least 3,000 years before Christ [1,2]. Its unique bright yellow colouring, malleability and ductility have seen it used for jewellery and decoration for thousands of years. It has also been used widely as currency, and is associated with wealth, royalty and religion [1,2]. The desire to possess gold has become an obsession for many, with Pindar, as early as the 5th century BC, describing it as "a child of Zeus, neither moth or rust devoureth it, but the mind of man is devoured by this supreme possession" [3]. The thousands that flocked to the gold fields in the rushes of the nineteenth and early twentieth centuries in the (usually futile) search for their fortune is an example of this. It inspired world exploration in the search for further goldfields and also discoveries, for example the alchemists attempts to turn base metals into gold became the beginnings of modern chemistry. Conversely, the greed generated by wealth and power gold can often bring, has led to much bloodshed and violence over the centuries [2].

Gold has been known since antiquity primarily through its low reactivity, which resulted in the existence of the native metal in the environment [1]. Until the late nineteenth century, the primary means of gold extraction was through the use of various gravity concentration procedures, relying on its high density (specific gravity of ~19.3 [4]). By 1400 AD, amalgamation with mercury was also used

widely in Europe [1], a process still utilised today in parts of the world to the detriment of its practitioners.

1.2 Cyanide Extraction

Despite significant improvements, gravity and amalgamation processes were found to be unsuitable for extracting fine gold or where the gold was associated with sulfide minerals, and this led to the search for alternative methodologies [1]. Between 1887 and 1888, the extraction of gold was revolutionised by MacArthur and the Forrest brothers through their patenting of what became known as the cyanide process [1]. Their method involved the dissolution of gold in an aerated alkaline cyanide solution, with extraction of the leached gold from solution by cementation with zinc. The ability to dissolve gold in cyanide solutions was not new, and had been reported as early as 1783 by Scheele [1]. Elsner in 1846 [5] investigated the dissolution of gold in aerated cyanide solutions and reported the reaction equation given in Eqn 1.1 which bears his name.

$$4Au + 8CN^- + O_2 + 2H_2O \rightarrow 4Au(CN)_2^- + 4OH^- \qquad (1.1)$$

This equation, while stoichiometrically correct, does not indicate the mechanism of the reaction which in more recent studies was been found to be more complex [1].

The achievement of MacArthur and the Forrest brothers was turning this chemistry into a workable hydrometallurgical process. The first plant to use the new technology was 'Crown Mine' in New Zealand which opened in 1889 [1], and the technique quickly established itself as the primary method for extracting

gold from its ores. The process has been significantly improved since its inception with for example, improvements in gold cementation using the Merrill-Crowe process, far greater understanding of the reaction mechanisms and since the 1970's, the replacement in many cases of cementation with carbon-based adsorbents for the extracted gold [1,6,7]. This has all resulted in the ability to economically mine far lower grades of gold than would ever have been thought possible 120 years ago.

1.3 Problems with Cyanide-Based Gold Leaching

While cyanide leaching of gold has been proven to be a robust and highly successful technique, as is evident by its widespread use, there are two main problems that have led to investigations into alternative leaching technology, the first being refractory ores and the second the toxicity of cyanide.

1.3.1 Refractory Ores

Cyanide does not handle certain types of ores particularly well, and these are described as 'refractory'. Such ores prevent economic cyanidation through one (or more) of three mechanisms [1,8,9]. The gold can be partially or wholly encapsulated in the host mineral which even fine grinding will not liberate, preventing surface contact between the gold and cyanide and therefore effective leaching. This occurs for example with some pyritic ores. Leaching can be ineffective or uneconomic for ores containing high concentrations of what are known as 'cyanicides', other substances in the ore that react with cyanide, such as copper, and some sulfide minerals. These substances result in unsustainably high cyanide consumption. The third mechanism involves carbonaceous ores, in which

the gold will leach effectively, however the gold cyanide complex will then absorb onto the carbonaceous material in the ore and be lost to tailings, in a process known as 'preg-robbing'. Development of pre-treatment procedures such as bio-oxidation, roasting, pressure oxidation and chemical oxidation have however been effective in making some of these ores amenable to economic cyanide leaching [1,8].

1.3.2 The Toxicity of Cyanide

The other problem that has dogged cyanide leaching in recent years is concerns over the well-known toxicity of this material. The adult lethal dose of sodium cyanide has been reported to be less than 250 mg [10], while a concentration of 270 ppm of hydrogen cyanide gas (generated by contact of cyanide salts with acid) in air is "immediately fatal" to humans [11]. The hazards associated with the use of cyanide in the mining industry received major world attention in 2000 with a tailings dam spillage at a gold mine in Baia Mare, Romania. Over 100,000 m^3 of cyanide laced water spilt into the Tisza River and eventually reached the Danube, killing tonnes of fish and poisoning the drinking water of over 2 million Hungarians [12]. The accident was labelled "the biggest environmental disaster in Europe since Chernobyl" [13].

While this has been the accident that has received the most publicity, there have been numerous cyanide-related accidents from gold mines over the years, of varying severity. Other post-1990 examples of spills that have occurred through tailing dam breaches, include the Summitville Gold Mine, Colorado, USA, in 1992 where a 25 km stretch of the neighbouring river was poisoned, leaving a clean-up bill in excess of US$100 million [14,15], and secondly at the Omai Gold

Mine, Guyana, in which 4.2 million m^3 of cyanide contaminated water was spilt into the Essequibo River causing a small fish kill and resulting in an 80 km stretch being labelled an "environmental disaster zone", although the actual lasting impact appears to have been minor [12]. Accidents have also occurred involving the transportation of cyanide to mining sites, such as in Papua New Guinea during 2000 where a helicopter lost a pallet containing ~1 tonne of sodium cyanide in the jungle in transit to the Tolkuma Gold Mine [16]. Numerous bird kills have also been reported, caused by poisoning from gold mine tailing dams. A highly publicised kill occurred in 1995 when 2,700 birds were poisoned at the Northparkes Gold Mine in New South Wales, due to inadequate monitoring of weak acid dissociable metal cyanide complexes in the tailings dam [11].

Because of the concern over cyanide usage, many governments are introducing legislation to restrict such processes, and in some cases ban its use altogether. The use of cyanide for gold leaching was banned by the state of Montana in 1998 after a public referendum, and several other states of the USA are reported to be considering similar legislation [6,16]. Communities near the ancient city of Pergamon, Turkey have been preventing the establishment of a gold mine nearby through protest and legal action for several years. Turkish courts in 1997 invalidated permits granted to the mining company involved, ruling that the use of cyanide contravened the country's constitutional guarantee to a healthy and intact environment in a case launched by these communities [17].

1.4 The Search for Alternatives

Because of the difficulties discussed in the previous section much time and effort has been spent examining alternative systems for leaching gold. The lixiviant systems that have been investigated include:

- Ammonia
- Bisulfite
- Bromine
- Chlorine
- Iodine
- Malononitrile and other nitriles
- Sulfide
- Thiocyanate
- Thiosulfate
- Thiourea

A more comprehensive list can be found in reference [18]. For some time thiourea was considered the most promising alternative but many process problems, primarily the poor stability, and suspected carcinogenicity of thiourea (highlighted by its addition to the California list of carcinogens during 1988). This has significantly reduced interest in this leaching system. A recent examination of alternative lixiviant systems for gold stated that this property of thiourea meant it should not be considered further for gold leaching [6]. At the present time leaching using thiosulfate is considered the most likely to provide a viable less-toxic alternative to cyanide [6].

1.5 Thiosulfate Leaching

1.5.1 Introduction

Interest in thiosulfate as a lixiviant for precious metals was initially centred around its ability to leach silver, and was known as the Patera process after von Patera who was the first to leach silver ores with sodium thiosulfate after a chloridising roast during the mid-nineteenth century. The process was also utilised

in South America in the first half of the twentieth century [19-21]. The ability of thiosulfate to dissolve gold under alkaline or near neutral conditions, in the presence of a mild oxidant, was reported in 1905 by White [18,21]. During 1978 interest in thiosulfate leaching was revived with Berezowsky, Sefton and Gormely [22] claiming a patent on the thiosulfate leaching of gold from the residues of an ammoniacal oxidation leach of sulfidic copper concentrates. Since then there have been numerous papers and patents published on the subject, recently reviewed by Aylmore and Muir [21].

Thiosulfate is considered a non-toxic material, the ammonium salt of which has been used as fertiliser and is a "generally recognised as safe", indirect and direct human food ingredient [23,24]. Whilst the process is significantly more environmentally friendly than cyanide-based leaching (although this has been disputed for example in [7,18]) this is not to say it is completely benign because of problems that may be generated by the other two reagents required for successful leaching, namely ammonia (volatile and corrosive at high concentrations) and copper(II) (toxic). Under certain environmental conditions thiosulfate can also be oxidised by sulfur oxidising bacteria, which can result in the generation of sulfuric acid, potentially causing problems in the case of a significant spillage [25-27].

Apart from its lower environmental impact, the thiosulfate process also has some properties that potentially offer advantages over cyanide for certain refractory ore types. Some examples of this are lower interference from unwanted base metal cations [21], and low adsorbitivity of the gold thiosulfate complex onto activated

carbon, making it less prone to preg-robbing in carbonaceous ores [21,28,29]. It is also considered potentially advantageous for high copper ores since the ore will provide the catalyst for leaching [19]

1.5.2 The Thiosulfate Leach Reaction

Modern thiosulfate leaching occurs in an ammoniacal solution containing copper(II) as catalyst, since the reaction using oxygen as oxidant is too slow under normal atmospheric conditions. The mechanism of the reaction is thought to proceed as shown in Equations 1.2 and 1.3 [21].

- Anodic Reaction:

$$Au + 2S_2O_3^{2-} \rightarrow Au(S_2O_3)_2^{3-} + e^- \quad (1.2)$$

- Cathodic Reaction:

$$Cu(NH_3)_4^{2+} + 3S_2O_3^{2-} + e^- \rightarrow Cu(S_2O_3)_3^{5-} + 4NH_3 \quad (1.3)$$

Some researchers argue that the gold actually enters solution as a gold ammine complex ($Au(NH_3)_2^+$), which thereafter converts to the more stable thiosulfate complex [30-32]. The copper catalyst is then regenerated through Eqn 1.4:

$$4Cu(S_2O_3)_3^{5-} + O_2 + 16NH_3 + 2H_2O \rightarrow 4Cu(NH_3)_4^{2+} + 12S_2O_3^{2-} + 4OH^- \quad (1.4)$$

From this, the overall leaching reaction can be represented by Eqn 1.5:

$$4Au + 8S_2O_3^{2-} + O_2 + 2H_2O \rightarrow 4Au(S_2O_3)_2^{3-} + 4OH^- \quad (1.5)$$

A broad range of reagent concentrations has been used with a recent review reporting extremes in the literature of 0.1-2 M for thiosulfate, 0.1-6 M for ammonia and 0.001-0.1 M for copper [21].

Since this abovementioned review, a patent has appeared which outlines a process for the reaction requiring little or no copper(II) and ammonia, instead using above

atmospheric concentrations of oxygen in the leaching vessel to increase the rate of gold dissolution [33]. The ramifications of this patent on the direction of research into thiosulfate leaching remain to be seen.

1.5.3 Problems Hindering Commercial Development of the Process

Despite its promise, and the large amounts of effort that has been spent researching the process, there are still several problems that are currently preventing it from being an economic alternative to cyanide. The leach chemistry is far more complicated than the cyanide system, is not as well understood and can show uneconomically high thiosulfate consumption. One problem with the leach is that the copper(II) catalyst reacts with the thiosulfate in the simplified reaction given in Eqn. 1.6 [21,34]

$$2Cu(NH_3)_4^{2+} + 8S_2O_3^{2-} \rightarrow 2Cu(S_2O_3)_3^{5-} + S_4O_6^{2-} + 8NH_3 \qquad (1.6)$$

The process is more complex in the presence of oxygen [35,36]. Tetrathionate can also then decompose via the reaction pathways given in Eqns. 1.7 to 1.9 [21,34,35].

$$S_4O_6^{2-} + S_2O_3^{2-} \rightarrow S_5O_6^{2-} + SO_3^{2-} \qquad (1.7)$$

$$S_4O_6^{2-} + SO_3^{2-} \rightarrow S_3O_6^{2-} + S_2O_3^{2-} \qquad (1.8)$$

$$S_5O_6^{2-} + 3OH^- \rightarrow \tfrac{5}{2}S_2O_3^{2-} + \tfrac{3}{2}H_2O \qquad (1.9)$$

Sulfate formation can also occur through copper(II) catalysed oxidation through for example Eqn 1.10 [35,37].

$$S_2O_3^{2-} + 2O_2 + 2OH^- \rightarrow 2SO_4^{2-} + H_2O \qquad (1.10)$$

Other metal ions such as iron(III) and some minerals are also known to catalyse the oxidation of thiosulfate, for example pyrite, most often to tetrathionate, [24,37-39]

Much has been attempted to minimise the thiosulfate consumption. The addition of sulfite [40,41] or sulfate [42,43] to the leach has been proposed, with the former subsequently used by a number of other researchers [23,44-50]. However, the utility of these techniques, and the use of sulfate in particular, has more recently been questioned [21]. The recent review of the gold thiosulfate literature stated that a build-up of sulfate was detrimental to the leach, while sulfite will lower the Eh of the solution and reduce copper(II), itself being oxidised to sulfate and/or dithionate [21].

Extraction of the leached gold from the system is also a more difficult proposition. The gold thiosulfate complex does not absorb well onto activated carbon [6,21,29] which although an advantage for carbonaceous ores, prevents the use of carbon-in-pulp technology employed in cyanide leaching. Cementation is also quite complex relative to cyanide leaching [6] and although described as "relatively successful on clarified liquors" [21] it would seem to be not an ideal recovery technique. Ion-exchange resins are considered the most promising means of extraction from thiosulfate leach liquors [37]. However, there are still difficulties with the use of these materials. One of the major problems is that the polythionates generated in the leach through thiosulfate oxidation can compete with the gold thiosulfate complex for sites on the resin [49,51], highlighted by a recent patent on the use of these ions for gold elution in thiosulfate systems [52].

1.5.4 Species Present in a Typical Leach

From the preceding discussion the important species in gold thiosulfate leach solutions are as follows:

- Thiosulfate.
- Ammonia.
- Polythionates, predominantly trithionate ($S_3O_6^{2-}$) and tetrathionate ($S_4O_6^{2-}$), generated from the oxidation of thiosulfate.
- Sulfate, generated by oxidation of thiosulfate and possibly also added as a starting reagent.
- Sulfite, if added as a starting material.
- Copper(I) and copper(II).
- Gold(I).
- Other leachable components of the ore.

Eh-pH diagrams relevant to the gold thiosulfate system have been constructed in an attempt to further understand the speciation of these solutions [19,21,52a]. However, the thiosulfate system is thermodynamically unstable, which combined with the complexity of the leach solutions makes it difficult to construct diagrams that reflect the actual speciation. For this reason Eh-pH diagrams have not been included in this review, and the reader is directed to the cited references for further detail of these investigations.

The actual speciation of the metals in solution is not known, although work to date suggests that $Au(S_2O_3)_2^{3-}$ ($\log\beta$=26-28 [21,53]) is the dominant, if not only, gold species present. $Au(S_2O_3)^-$ is known to exist but this is less stable than the bis complex [54], and no thermodynamic data could be found for this species. Suggestions, based on thermodynamic studies, that the gold(I) diammine complex $Au(NH_3)_2^+$ ($\log\beta$ between 13-26 having been reported [21]) will predominate in solutions at pH values higher than 8.5 with an ammonia concentration higher than

0.1 M have not agreed with experimental data [21]. Another paper [19] has recently also questioned the accuracy of the earlier thermodynamic calculations, finding no stability region for the ammine complex with the difference in Eh-pH diagrams attributable to the use of a different free energy of formation value for thiosulfate. The possibility of gold(I) hydroxide complex formation in leach liquors has not been considered, although there is a reference to the existence of $Au(OH)_2^-$ ($\log\beta \sim 25.0$) in aqueous solutions [54a].

The chemistry of the copper in solution is complicated due to the copper(I)/copper(II) redox couple and the fact that copper(I) forms both significantly stable thiosulfate and ammonia complexes [21,37]. The copper(II) chemistry is dominated by the well known copper tetraammine ($Cu(NH_3)_4^{2+}$) complex, although the triammine species has been suggested as being be the primary oxidising species [35,37]. The main copper thiosulfate species in solution is thought to be $Cu(S_2O_3)_3^{5-}$ but at lower thiosulfate concentrations (<0.05 M), $Cu(S_2O_3)_2^{3-}$ is expected to predominate [37]. Mixed thiosulfate-ammonia copper complexes may also exist in the leach solutions but have not been reported in the literature to date [37]. The copper(I) monothiosulfate complex is insoluble in water [55], while high copper concentrations in solution can result in precipitation of mixed copper-ammonia-thiosulfate salts [21].

Several other metals are known to have appreciably stable complexes with thiosulfate and/or ammonia, [37], although it has been stated that in general thiosulfate allows a decreased interference from foreign cations in comparison with cyanidation [21]. Dissolution of iron has been identified as a problem at pH

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values < 8 [45], and a comparison of several lixiviant systems for leaching of gold from an almost fully oxidised low grade ore noted the presence of a significant quantity of nickel in the waste thiosulfate liquor [7].

Some studies demonstrate the capability of thiosulfate leaching to decompose some sulfide minerals such as chalcopyrite, pyrrhotite, arsenopyrite and to a lesser degree pyrite [39,42], although contrary to this it has also been reported that pyrite is not leached significantly by these leach solutions [56]. Copper sulfide minerals other than chalcopyrite are readily dissolved in thiosulfate leach solutions [21].

There is a subsequent need for a detailed investigation into the analytical chemistry of gold thiosulfate leach solutions. The following section will evaluate the current state of the art of sulfur-oxygen species analysis

1.6 The Analytical Chemistry of the Sulfur and Sulfur-Oxygen Species

1.6.1 Introduction

Aqueous mixtures of sulfur and sulfur-oxygen species have traditionally been a difficult group of compounds to analyse. The chemistry that occurs in such solutions is quite complex since certain species can react with each other, decompose or become oxidised by air [57-60]. Sample storage can result in the occurrence of compositional changes which may produce erroneous results in the subsequent analysis [61,62]. Sometimes the analytical technique used may itself perturb the composition of the mixture [63,64].

Many analytical techniques have been used to determine sulfur ions. Wet chemical methods exist for most of the sulfur-oxygen species [58,59,65] and some sulfur speciation studies using these techniques have been reported [26,27,66-68]. The main disadvantage of wet chemical methods is that they are time-consuming and generally only applicable to the determination of one analyte ion at a time. UV-visible spectroscopy has also been applied, [58,59] often attaining detection limits in the 10^{-6} M range, although methods using this technique suffer similar problems to wet chemistry, particularly the restriction of being applicable to one analyte at a time. Speciation studies by UV-visible spectroscopy [69-75] are generally specific to samples containing only certain sulfur anions and this limits their application. Electrochemical techniques such as polarography and voltammetry can determine two or three species in a single scan [76-85], but even here multiple analyses are again usually required for detailed speciation studies. Very low detection limits (for example 10^{-8} M) are possible for some species using these methods, with the main application being the study of sulfur compounds (particularly sulfides) in natural waters. Fourier transform infra-red (FTIR) spectroscopy [86], attenuated total reflectance (ATR) FTIR spectroscopy [87] and Raman [63,88] spectroscopy can be used for the simultaneous determination of a greater number of sulfur species in solution. Generally the disadvantage of these methods is their detection limits, typically in the range 10^{-4}-10^{-2} M, which are much higher than for most other instrumental techniques. Finally, flow injection systems have also been utilised for sulfur speciation [89,90] although detection limits were again reasonably high, falling in the 10^{-5}-10^{-4} M range.

Separation techniques such as ion-chromatography (IC) and capillary electrophoresis (CE) can be used to determine more sulfur species in a single analysis than is possible by most other analytical procedures, with detection sensitivity generally between 10^{-7}-10^{-5} M. Separation is particularly important for the polythionates ($S_xO_6^{2-}$), which have similar chemical properties and are therefore inherently difficult to determine in mixtures.

This review will therefore concentrate on the separation science literature for the determination of elemental sulfur (S_8, also denoted S^0), sulfide (S^{2-}), polysulfides (S_x^{2-}, $x \geq 2$), sulfite (SO_3^{2-}), sulfate (SO_4^{2-}), thiosulfate ($S_2O_3^{2-}$), dithionate ($S_2O_6^{2-}$), the polythionates ($S_xO_6^{2-}$, $x \geq 3$) and the metal-thiosulfate complexes ($M_m^{x+}(S_2O_3)_y^{(mx-2y)}$) in aqueous solutions. The focus is on sulfur speciation (separations of three or more sulfur anions), rather than the determination of a single sulfur or sulfur-oxygen ion. A brief description of the separation techniques used in this project, namely ion-chromatography, capillary electrophoresis and isotachophoresis is also given.

1.6.2 Chemistry of Sulfur Species Influencing their Analysis

The chemistry of sulfur species in aqueous mixtures can be very complex, with many species readily taking part in redox and nucleophilic displacement reactions resulting in compositional changes over time [57,60,91,92]. These factors can create difficulties in accurately quantifying all sulfur species in solution, regardless of the method used. Separation science techniques are no exception and for this reason a summary of the major reactions and problems that can affect the determination of these anions is outlined.

Accurate determination of sulfite in aqueous solution has been problematic due to the ease with which it is oxidised by air to sulfate. This oxidation is mediated by free radicals and catalysed by redox-sensitive transition metal ions, such as iron(III) and copper(II), and occurs most rapidly in acidic solutions [57,91,93]. Purging solutions with nitrogen or argon does not completely prevent sulfite oxidation [94] and oxidation has been reported to occur during a chromatographic separation due to oxygen permeating through the PTFE tubing used in the system [95]. In this study the fraction of sulfite oxidised was also found to be dependent on such factors as the retention time, the amount of iron(III) or copper(II) present in the sample, the chromatographic column, and even on the concentration of sulfite in the sample. To prevent sulfite oxidation, pre-analysis derivatization methods have been developed, with the most widely reported technique being the addition of formaldehyde [57,93-99], which reacts with sulfite via the reactions [57]:

$$\underset{\text{Formaldehyde}}{H_2C=O} + H_2O \rightarrow \underset{\text{dihydroxymethane}}{H_2C(OH)_2} \qquad (1.11)$$

$$H_2C(OH)_2 + HSO_3^- \rightleftharpoons \underset{\text{hydroxymethanesulfonate}}{H_2C(OH)(SO_3)^-} + H_2O \qquad (1.12)$$

The addition product, hydroxymethanesulfonate, formed in reaction (1.12) dissociates in alkaline media, which makes this approach ineffective for basic samples. However, it can be used to prevent, or at least reduce, sulfite oxidation in acidic samples, prior to injection into an alkaline eluent. The time in which sulfite is reported to be stable in the presence of formaldehyde varies widely from 90 min [96,98] to 2 weeks [93]. This may be attributable to differences in experimental conditions, such as formaldehyde concentration and solution pH. If

the eluent used has a pH of less than 10.7 the sulfite present will at least partially exist as hydroxymethanesulfonate. This has a significantly lower retention time than sulfite in IC [93,100-102], and can result in co-elution problems with other monovalent anions such as chloride. For capillary electrophoretic systems, the mobility of the addition product is significantly lower than for sulfite [103]. The formaldehyde method has also been questioned by some authors, since it has been demonstrated that the peak area obtained is dependent on the formaldehyde/sulfite ratio [96,100].

Sulfite stabilising agents other than formaldehyde have also been investigated and include other aldehydes and ketones such as acetone [93,100,103], formic acid [102], isopropanol [94,100,104], methanol [93], ethanol [93,103], propanol [103], glycerine [105], glycerol [93,94,100,103,106], ethylene glycol [103], fructose [94,100,103], glucose [100] and mannose [100]. Ethanol, glycerol, propan-2-ol, glucose and fructose have been identified as being ineffective as stabilisers [93,94,100] while methanol and acetone do not preserve sulfite in solutions containing iron(III), manganese(II) or copper(II) ions [93]. De Carvalho and Schwedt found propanol to be superior to formaldehyde and a variety of other stabilisation agents in their study of sulfite oxidation [103]. Hassan [107] has reported that the addition of EDTA and L-ascorbic acid to the chromatographic eluent reduces on-column sulfite oxidation to negligible levels. The addition of these reagents prevents the metal ions present in the solution from catalysing the oxidation reaction. Stock solutions prepared in such an eluent were reported as being stable to oxidation over a one-month period.

Sulfide is another species that will rapidly undergo oxidation in air, particularly in the presence of heavy metals or on exposure to light, with the dominant product being elemental sulfur, although oxyanions such as sulfate may also be produced in smaller quantities [91]. Oxidation can be minimised by purging oxygen from solutions containing sulfide. The anti-oxidants mannitol and ascorbic acid, as well as organic solvents such as acetonitrile and 2-propanol have been examined as stabilising agents for sulfide in Kraft process liquor samples, although all were found to be ineffective [62]. This result contradicts earlier work [106] in which successful stabilisation of sulfide in these liquors with ascorbic acid was reported. Freezing of samples for storage prior to analysis also failed to prevent oxidation, although this was attributed in part to interactions between the sulfide and lignin in the Kraft liquor samples under investigation that precipitated during freezing [62].

Another difficulty associated with the determination of sulfide is that it can be readily converted to hydrogen sulfide (H_2S) in acidic solutions and can then be lost to the atmosphere. This results in low sulfide recoveries, particularly if the solution is being purged of oxygen by displacement with an inert gas. Storage of samples in alkaline solution is therefore recommended for this anion, with some methods adding carbonate to solutions containing S^{2-} to prevent volatilisation [96,98]. Sulfide forms precipitates with many metals, which can also hinder quantitative analysis. Hissner *et al.* [102] observed problems with the sulfide peak area reproducibility during ion-chromatographic analysis, obtaining low results for the first few injections of a sample run. This was partly due to precipitation of sulfide with heavy metal ions accumulated on the head of the

column from metallic components of the chromatographic system. A resultant black layer of sulfide precipitate was observed at the head of the column after several injections. Reproducibility was improved by injecting a high concentration sulfide solution twice prior to sample analysis, which precipitated any heavy metals present in the system.

Thiosulfate oxidation to sulfate (via tetrathionate) is slow, except in the presence of oxidants such as copper(II), iron(III) or iodine (I_2) [57]. A reduction in thiosulfate oxidation catalysed by transition metals has been observed with the addition of Na-Amberlite CG-120 cation-exchange resin to samples [57]. A refrigerated 100 μM thiosulfate/1 mM iron(III) solution lost 12.5 μM thiosulfate over 6 weeks in the presence of the cation-exchange material, compared to almost complete loss in 1 week if formaldehyde was added to the solution with no cation exchange resin and 95% loss in 4 h if no treatment was applied. Thiosulfate additionally decomposes to sulfite and elemental sulfur in weakly acidic solutions [57,91] through a nucleophilic displacement reaction:

$$8HS_2O_3^- \rightarrow S_8 + 8HSO_3^- \qquad (1.13)$$

The products of the decomposition are different in solutions of high or moderate acidity and can include polythionates, sulfate, sulfide and sulfur-containing oils [60,91].

Polythionates, thiosulfate and sulfite interact in aqueous solutions through the equilibrium:

$$S_xO_6^{2-} + S_2O_3^{2-} \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} S_{x+1}O_6^{2-} + SO_3^{2-} \qquad (1.14)$$

which proceeds via nucleophilic displacement reactions [57,60,91,92]. This equilibrium is pH dependent and at neutral pH favours the left-hand side of the equation. The lower polythionates also react with sulfide as follows [59,108,109]:

$$S_xO_6^{2-} + S^{2-} \rightarrow (x-3)S + 2S_2O_3^{2-} \quad (x = 3,\ 4,\ 5,\ 6) \qquad (1.15)$$

The extent to which this reaction occurs is again dependent on the pH of the solution.

The stability of the polythionates ($x = 4$ to 6) in acidic solutions (pH 0-2) has been studied [61] and storage conditions were found to exert some influence on the rate of polythionate decomposition, such as the type of bottle used and the storage temperature. Formaldehyde, oxalaldehyde and hydroxylamine hydrochloride (HAH) were examined as stabilising reagents. Formaldehyde and oxalaldehyde were found to disturb the polythionate speciation of solutions by shifting the equilibrium given in equation 1.14 to the right through complexation with the sulfite. Concentrations of formaldehyde higher than ~0.4% were also found to accelerate the decomposition of tetrathionate, but HAH enhanced the stability of tetrathionate, pentathionate and hexathionate, maintaining the initial distribution of these ions for three weeks even in the presence of oxygen. The iron(III)-catalysed oxidation of thiosulfate was found to increase the rate at which polythionate speciation was altered, favouring lower chain lengths. This process was detectable after 60 h.

Polythionates with four or more sulfur atoms are unstable under alkaline conditions [60,91,92,110,111], although the reaction products are again dependent upon solution conditions. An investigation by Zou *et al.* [112] examined the

stability of polythionates (x = 3 to 5) in a neutral to slightly alkaline ion-interaction chromatography eluent (24:76 acetonitrile (ACN)-water containing 3 mM tetrabutylammonium hydroxide (TBAOH) and 0.5 mM Na_2CO_3). Trithionate was stable in this eluent at pH 8, whilst the tetra and pentathionate concentrations decreased significantly within a few hours due to decomposition, with the decomposition rate increasing with pH. Despite these observations, the possible decomposition or change in speciation over the course of a chromatographic or electrophoretic run has not yet been investigated.

The preceding paragraphs highlight the problems inherent in storing solutions containing sulfur species prior to analysis. There appears to be no guaranteed method of ensuring that the initial sulfur speciation of a sample will be preserved on storage. The use of stabilisers reduces the reaction of individual sulfur species in solution, although the stabilisers themselves can perturb the concentrations of other ions. Results in the literature suggest that there is no substitute for immediate analysis of samples containing mixtures of sulfur species.

1.6.3 Ion-Chromatographic Determination of Sulfur Species

1.6.3.1 Introduction [113,114]

IC, is a physico-chemical separation technique that utilises differences in the distribution of ionic solutes between a mobile and stationary phase. Using the modern version of the technique, a sample mixture of ionic solutes is injected into a liquid flow stream known as the eluent which is then passed through a "column", usually a metal or plastic cylinder packed with uniform, small-diameter (e.g. 5 μm) particles. The cylinder itself is usually between 5-30 cm long with an internal diameter of between 2-9 mm., and the particles are held stationary inside

by means of porous frits at both ends. A high pressure pump is required to drive the solution through the column, and a flow through detector is placed at the far side to detect the components as they elute from the column. A typical configuration for an ion-chromatograph is shown in Fig. 1.1.

The mechanism of separation is dependent on the branch of IC used. In ion-exchange chromatography, the column packing is a resin, which can be inorganic or a polymeric organic material that contains fixed charged groups on its surface. Where the fixed charge is positive, the resin is said to be an anion-exchanger, for fixed negative charges it is said to be a cation-exchanger. Associated with the fixed charge are counter-ions of opposite charge to render the resin neutral. The process of ion-exchange will be illustrated by considering an anion-exchange resin. Consider a resin in water with fixed positive charge (R^+) and counter ion (E^-). If another counter ion (A^-) comes in contact with the resin an equilibrium is established as shown in Eqn 1.16.

$$R^+E^- + A^- \rightleftharpoons R^+A^- + E^- \qquad (1.16)$$

This process is stoichiometric and can be generalised to ions with charge >1. The equilibrium constant for the process is known as the selectivity coefficient which can be expressed as shown in Eqn 1.17:

$$K_{A,E} = \frac{(A_R^{x-})^y (E_M^{y-})^x}{(A_M^{x-})^y (E_R^{y-})^x} \qquad (1.17)$$

where x and y denote the charge on A and E, the parentheses indicate the activity

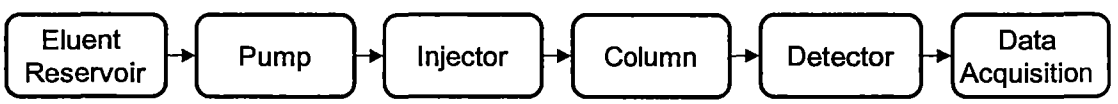

Fig. 1.1 Essential features of an ion-chromatographic system.

of each species and R and M refer to the resin and mobile phases respectively. In anion-exchange chromatography, separation between two anions A^- and B^- occurs via the use of the eluent, which consists of an ionic solution with anion (E^-). The separation of the two solute ions occurs as a result of the different selectivity co-efficients that exist between the eluent anion and each sample anion. The mechanism for cation-exchange materials is analogous.

Another branch of IC is ion-interaction chromatography, for which the mechanism is more complex. The instrumentation is identical, but a reverse-phase HPLC column is used and the eluent contains what is known as an "ion-interaction" or "ion-pair" reagent, which in the case of anion analysis is usually a strong base cation such as a tetraalkylammonium ion. Three models have been proposed for the mechanism of separation in ion-interaction chromatography, but only the "ion-interaction" model, that considered to best represent the observed experimental data, will be discussed here.

According to this model (represented in Fig 1.2), the hydrophobic ion-interaction reagent absorbs onto the stationary phase surface in a dynamic equilibrium with the eluent, in turn inducing formation of an electrical double-layer. In the case of anion analysis, an evenly spaced positively charged primary layer at the stationary phase surface is the result, followed by a second, diffuse layer of counter-ions. Analyte ions (anions will be considered here), can compete with sites in the negatively charged secondary layer, and once inside electrostatic attraction and also possibly solvophobic (reverse phase chromatography) effects will usually result in it moving into the primary layer. This disrupts the electroneutrality of

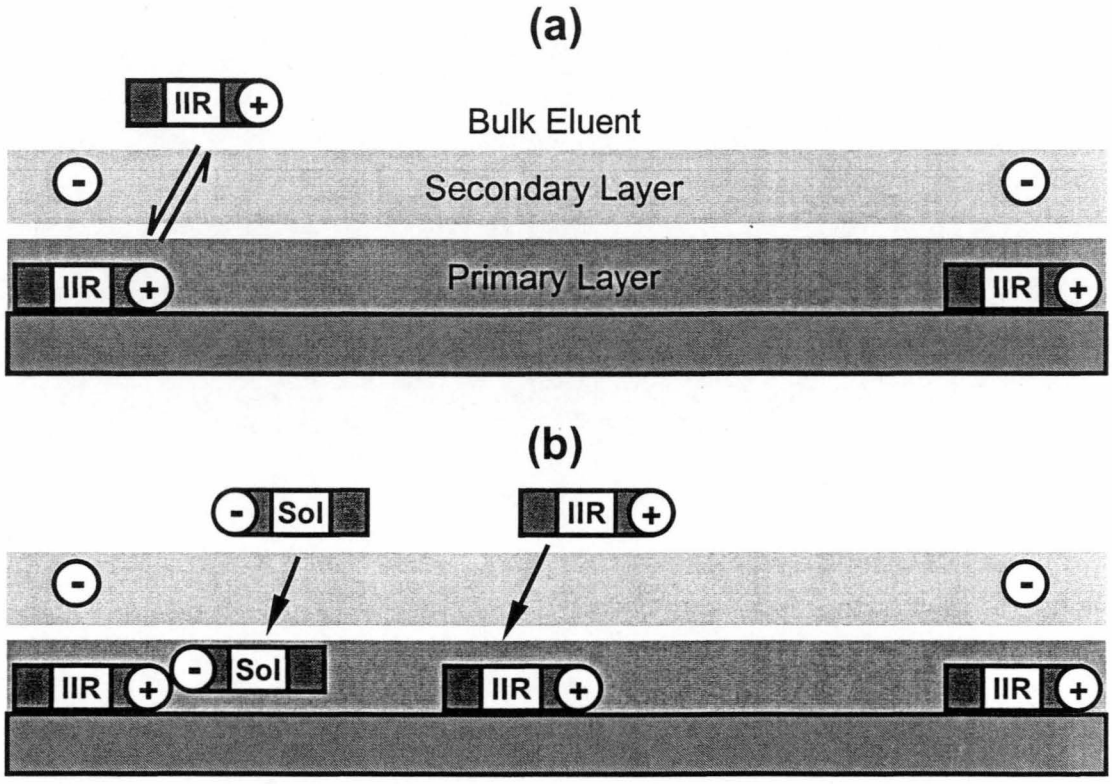

Fig. 1.2 Illustration of the ion-interaction mechanism. (a) Equilibrium of ion-interaction reagent onto stationary phase (b) Retention mechanism of a solute anion. Extracted from [113].

the layer, and therefore another ion-interaction cation is drawn into the primary layer, meaning that the retention process involves a pair of ions. Separation occurs as a result of competition between the different analyte anions and the counter-ion of the ion-interaction reagent (the eluent anion in this system) for sites in the double layer.

IC methods have become very popular for the determination of many sulfur anions. In the literature up to 1988 sulfate was the second most frequently analysed anion by such methods, surpassed only by chloride. Sulfite and thiosulfate were the ninth and tenth most frequently analysed anions respectively and sulfide was in the top 20 [113]. Documentation of every paper and application note on the determination of sulfur species such as sulfate and sulfite is not feasible due to the large number of references involved. The reader is therefore directed to books on IC [113] and the catalogues and information sheets produced by column manufacturers, for example [115], to obtain more detailed information on the separation of common ions such as sulfate. In this review the primary focus will be on separations involving multiple sulfur and sulfur-oxygen species.

1.6.3.2 Early (Classical) Ion-Exchange Methods

Prior to the development of the instrumentation discussed in the previous section, IC was performed using larger resin particles packed in vertical glass columns. The eluent moved through the column under the force of gravity and left the column through a stopcock that was used to regulate the flow rate. The eluate was collected in a series of containers, which were analysed using wet chemical or

other techniques. The first reported separation methods for sulfur-oxygen ions used such methodology.

Iguchi [116] separated dithionate and the polythionates (trithionate, tetrathionate, pentathionate) on Dowex 1-X2 anion-exchange resin using progressively higher hydrochloric acid concentrations (between 1 and 9 M). In a separate study [117] sulfate, sulfite, thiosulfate and sulfide were separated on Mitsubishi Kasei Diaion SA 100, a strongly basic quaternary ammonium polymer resin. Three ammonium nitrate eluents, a 0.1 M solution of 30:70 acetone-water adjusted to pH 9 with ammonia, an aqueous 0.1 M solution and an aqueous 1 M solution were required to complete the separation. Pollard *et al.* [118] attempted to separate sulfite, thiosulfate, trithionate, tetrathionate, pentathionate and hexathionate using De-Acidite FF resin cross-linked with 2% divinylbenzene (DVB). Sulfite and thiosulfate were eluted using 2 M potassium hydrogenphthalate, although a complete separation was not achieved. The polythionates were separated using 3 to 9 M hydrochloric acid. Schmidt and Sand [119] also separated the same mixture using sodium chloride in conjunction with hydrochloric acid eluents, however hexathionate could not be separated due to on-column decomposition.

Thiosulfate has been used as an eluent in classical ion-exchange chromatography to separate metal ions by utilising the formation of metal-thiosulfate complexes. One of the earliest papers by Vasil'ev *et al.* [120] reported the separation of copper(II)/zinc(II) and copper(II)/cadmium(II) binary mixtures on Wofatit P resin in the sodium form. In later papers [121,122] the retention of several metal ions on Amberlite IR-120 cation-exchange resin in the sodium form was studied.

Majumdar and Mitra [122] absorbed metal ions onto the head of the column and then eluted these by stepwise increments of sodium thiosulfate concentration ranging from 0.02 M to 0.5 M. Metal ions that formed significant anionic complexes with thiosulfate were eluted much earlier than other metal ions. Eusebius *et al.* [123] performed a similar but more detailed study using Dowex 50W-X8 cation-exchange resin in the H^+ form. Distribution coefficients of the metals in alkaline sodium thiosulfate solutions were determined over the concentration range 0.02 to 0.28 M. The same group had earlier examined the use of sodium thiosulfate eluents on Dowex 1-X8 anion exchange resin in the chloride form [124]. Those metal ions that showed significant formation of anionic complexes with thiosulfate, such as lead(II), copper(II) and silver(I) were eluted later than the remainder. The authors noted precipitation of copper(II), lead(II) and silver(I) sulfide in mixtures of these metals containing relatively low levels of thiosulfate.

The above procedures for the separation of metallo-thiosulfate complexes were only able to separate at best five complexes in any one analysis [122]. The ability of more modern instrumental chromatographic techniques and stationary phases to separate metallo-thiosulfate complexes is unknown since there are no published papers on the subject to date.

1.6.3.3 Modern Ion-Chromatography

Modern anion-exchange and ion-interaction chromatographic methods have been the most extensively applied separation techniques for the determination of sulfur anions, with selection of the particular technique being dependent on the nature of

Table 1.1 Anion-exchange chromatographic methods for the determination of sulfur species.

Species Detected	Sample	Sample Preparation	Column	Eluent	Detection	Detection Limit	Ref.
S^{2-}, SO_3^{2-}, SO_4^{2-}	Standards	-	Dionex HPIC-AS4 and AG4 guard	14.7 mM ethylenediamine, 10 mM NaH_2BO_3, 1 mM Na_2CO_3.	Suppressed conductivity and amperometry	Low ppb (sub µM)	[125]
S^{2-}, SO_3^{2-}, SO_4^{2-}	Kraft process (Green) liquors	Dilution, filtration through a Millex filter, addition of antioxidants ascorbic acid and glycerol.	Waters IC Pak A	5.0 mM H_3PO_4 (pH 6.5 with LiOH)	Non-suppressed conductivity	-	[106]
S^{2-}, SO_3^{2-}, $S_2O_3^{2-}$	Hot spring water	Degassed water and CO_3^{2-} to stabilise S^{2-} and formaldehyde to stabilise SO_3^{2-}, filtration and dilution.	Dionex HPIC-AS4A with AG4A guard	5 mM Na_2CO_3	PCR, UV (330 nm)	1.8-3.5 µM	[96]
S^{2-}, SO_3^{2-}, $S_2O_3^{2-}$	Human serum	Various pretreatments to reduce matrix followed by derivatisation with MBB. For serum samples SO_3^{2-} and S^{2-} analysis separate to $S_2O_3^{2-}$.	Macherey-Nagel Nucleosil 5N$(CH_3)_2$ with Nucleosil 100-5 C_{18} guard	3:13 ACN:CH_3COOH (pH 3) containing 25 mM $NaClO_4$	Fluorescence	20-40 nM	[126]
S^{2-}, SO_3^{2-}, $S_2O_3^{2-}$	Molten caustic desulfurised coal process solutions	Degassed water for S^{2-} and polysulfide standards.	Dionex HPIC-AS3	50-200 mM KNO_3, 5-10 mM NaOH. Flow rate gradient.	Sampled DC polarography	-	[127]
S^{2-}, SO_3^{2-}, $S_2O_3^{2-}$	Hot spring water	Degassed water and CO_3^{2-} in standards to stabilise S^{2-} and $S_2O_3^{2-}$, formaldehyde to stabilise SO_3^{2-}, dilution.	Tosoh TSKgel IC-anion-PW	15:85 ACN:H_2O containing 6.0 mM Na_2CO_3	PCR, indirect UV (350 nm)	2.8-48 µg/L (29-600 nM)	[98]
S^{2-}, SO_3^{2-}, $S_2O_3^{2-}$	Bacterial sulfur degradation solutions	Filtration, stabilisation of SO_3^{2-} with formaldehyde, standards degassed.	Alltech Durasep A-2	5:95 MeOH:H_2O containing 2.9 mM Na_2CO_3, 2.6 mM $NaHCO_3$, 1.3 mM *p*-cyanophenol (different concentrations of components used for analysis of samples)	Pulsed amperometry	0.02-0.3 mg/L (not specified for SO_3^{2-}) (0.2-9.4 µM)	[102]
S^{2-}, SO_3^{2-}, $S_2O_3^{2-}$	Waste water	-	TSK gel IC-anion-PW	0.1 M NaH_2PO_4-H_3PO_4 (pH 2.30)	Amperometry	-	[128]

Table 1.1 (Cont.)

Species Detected	Sample	Sample Preparation	Column	Eluent	Detection	Detection Limit	Ref.
S^{2-}, SO_4^{2-}, $S_2O_3^{2-}$	semi-lean MDEA used for gas treatment	Filtration and dilution	Dionex AG9-SC and AS9-SC in series	1.8 mM Na_2CO_3, 1.7 mM $NaHCO_3$	Suppressed Conductivity	-	[129]
SO_3^{2-}, SO_4^{2-}, $S_2O_3^{2-}$	Dithionite decomposition solution	-	Waters IC-PAK	10:90 ACN- 0.02 mM (1,3,6 or 7)-sodium NTS	Indirect UV (280 nm)	-	[130]
SO_3^{2-}, SO_4^{2-}, $S_2O_3^{2-}$	Standards	-	Glass column packed with Bio-Rad Bio-Rex 5 resin. Guard used.	25:30:45 Acetone:EtOH:H_2O containing 0.1 M $NaBO_2$ and 0.1 M $NaNO_3$ (pH 8.0). To elute SO_4^{2-} and $S_2O_3^{2-}$ 0.1 M $NaBO_2$, 0.2 M $NaNO_3$ in H_2O was used (pH 9.0).	PCR, UV (335 nm)	~0.05-0.1 mM	[131]
SO_3^{2-}, SO_4^{2-}, $S_2O_3^{2-}$	Standards	-	Dionex HPIC-AS5 and AG4 guard	2.8 mM $NaHCO_3$, 2.2 mM Na_2CO_3, 100 mg/L *p*-cyanophenol	Suppressed conductivity	Low ppb (sub µM)	[125]
SO_3^{2-}, SO_4^{2-}, $S_2O_3^{2-}$	Standards	-	Dionex AS-4A and AG4A guard	0.75 mM $NaHCO_3$, 2 mM Na_2CO_3	Suppressed conductivity	15-75 µg/L (0.16-0.94 µM)	[132]
SO_3^{2-}, SO_4^{2-}, $S_2O_3^{2-}$	Standards	Stabilisation of SO_3^{2-} using formaldehyde.	Vydac 302 or 300 IC	1-3 mM phthalic acid (pH 5-6 with NaOH)	Indirect UV (290 nm) or refractive index	10-250 µM	[94]
SO_3^{2-}, SO_4^{2-}, $S_2O_3^{2-}$	$Na_2S_2O_3$	-	Unknown	1-5mM glutamic acid (pH 9-11) or 5.6 mM Na_2CO_3 and 4 mM NaOH.	Non-suppressed conductivity	0.01-1 mg/L (0.1-9 µM)	[133]
SO_3^{2-}, SO_4^{2-}, $S_2O_3^{2-}$	Bacterial sulfur degradation solutions	Filtration, stabilisation of SO_3^{2-} with formaldehyde, standards degassed.	Vydac 302IC4.5	3 mM phthalate (pH 4.0)	Non-suppressed conductivity	0.6-3 mg/L (6.2-27 µM)	[102]
SO_3^{2-}, SO_4^{2-}, $S_2O_3^{2-}$	Standards	-	Two Dionex AG1 guard columns	$NaHCO_3$, Na_2CO_3 step gradient	Suppressed conductivity	-	[134]
SO_3^{2-}, SO_4^{2-}, $S_2O_3^{2-}$	Refinery accumulated water	-	Wescan 269001 anion	5 mM phthalate (pH 3.8)	Non-suppressed conductivity	-	[135]

Table 1.1 (Cont.)

Species Detected	Sample	Sample Preparation	Column	Eluent	Detection	Detection Limit	Ref.
SO_3^{2-}, SO_4^{2-}, $S_2O_3^{2-}$	Simulated industrial waste water	Filtration and dilution	Dionex AG17 and AS17 in series	1 to 40 mM KOH gradient	Suppressed conductivity	-	[136]
SO_3^{2-}, SO_4^{2-}, $S_2O_3^{2-}$	Kraft black liquor	-	Dionex AS11	40:60 MeOH:H_2O with a 30 to 60 mM NaOH gradient	Suppressed conductivity	-	[137]
SO_3^{2-}, SO_4^{2-}, $S_2O_3^{2-}$	Kraft process (black) liquors	Dilution with degassed water, filtration, stabilisation of SO_3^{2-} with formaldehyde.	Dionex AS-3	3.0 mM $NaHCO_3$, 2.4 mM Na_2CO_3	Suppressed conductivity and amperometry	-	[138]
$S_2O_3^{2-}$, SO_3^{2-}, SO_4^{2-}	Kraft process liquors	Dilution, stabilisation of SO_3^{2-} in standards by isopropanol.	OmniPax-100 with guard	1.3 mM Na_2CO_3, 6 mM NaOH, 1.58 mM *p*-cyanophenol	Suppressed conductivity	-	[104,139]
(a) S^{2-} (b) SO_3^{2-}, SO_4^{2-}, $S_2O_3^{2-}$	Kraft liquors	(a) Metal ion removing precolumn. (b) -	Dionex (a) HPIC-AS2, AS3, AS4A or AS5 with AG4 guard (b) HPIC-AS-5 and HPIC-AG4 guard	(a) 0.25 mM Na_2CO_3, 5 mM NaOH, 1.5 mM ethylenediamine (b) 1 mM Na_2CO_3, 5 mM NaOH, 0.8 mM *p*-cyanophenol.	(a) UV (215 nm) or pulsed amperometry (b) Suppressed conductivity	-	[140,141]
SO_3^{2-}/SO_4^{2-} (co-elute), $S_2O_3^{2-}$, S^{2-}	Coal plant process samples	Dilution	Glass column packed with VYDAC SAX resin. Guard used.	Phosphate gradient with (A) H_2O and (B) 1 mM Na_2HPO_4	PCR, UV (335 nm)	~0.05-0.1 mM	[131]
S^{2-}, SO_3^{2-}, SO_4^{2-}, $S_2O_3^{2-}$	Oil-shale retort by-product and other waste waters	Stabilisation of SO_3^{2-} with formaldehyde, degassing and dilution.	Bio-Rad Bio-Gel TSK IC-anion-PW resin based ion exchanger with TSK hydrophilic guard	12:88 ACN:1.2 mM potassium gluconate, 1.3 mM sodium borate, 40 mM boric acid, 54.2 mM glycerol, 0.02 mM EDTA (pH 7.2-7.6 with HNO_3 or KOH)	Non-suppressed conductivity, direct (254 nm), or indirect UV (265 nm) and/or amperometry	-	[101]
S^{2-}, SO_3^{2-}, SO_4^{2-}, $S_2O_3^{2-}$	Sediment samples spiked with sulfide	Centrifugation and filtration	Waters IC-Pak A with guard	0.5:2:12:85.5 glycerol:*n*-butanol:ACN:Borate-gluconate buffer (pH 8.5) containing 0.05 mM EDTA and L-ascorbic acid	UV (227 nm), conductivity (for SO_4^{2-})	~1-200 µg/L (10.4 nM-2.5 µM)	[107]

Table 1.1 (Cont.)

Species Detected	Sample	Sample Preparation	Column	Eluent	Detection	Detection Limit	Ref.
S^{2-}, SO_3^{2-}, SO_4^{2-}, $S_2O_3^{2-}$	Standards	-	Dionex 'fast-run' column.	Gradient elution using various mixtures of $NaHCO_3$, Na_2CO_3 and NaOH	Amperometric	-	[142]
S^{2-}, SO_3^{2-}, SO_4^{2-}, $S_2O_3^{2-}$	Kraft process (black) liquors	Dilution	Dionex Anion Separator	3.0 mM $NaHCO_3$, 2.4 mM Na_2CO_3	Suppressed conductivity and amperometry	-	[143-146]
S^{2-}, SO_3^{2-}, SO_4^{2-}, $S_2O_3^{2-}$	Standards	-	Dionex AS12A with AG12A guard	Step gradient from 60 mM to 100 mM NaOH	ICP-MS	35-270 µg/L (1.1-2.5 µM)	[147]
SO_4^{2-}, S^{2-}, SO_3^{2-}, $S_2O_3^{2-}$	Standards	-	Oka-1 resin packed column	5 mM Na_2CO_3	Suppressed conductivity and PCR indirect visible (522 nm)	0.01-0.05 mg/L (not specified for SO_4^{2-}) (0.32-0.62 µM)	[148]
S^{2-} (indirectly), SO_3^{2-}, SO_4^{2-}, $S_2O_3^{2-}$	Tannery Wastewater	Storage in NaOH (pH13), dilution and filtration. Portion of sample treated with NH_3/H_2O_2 solution and analysed separately for total S as SO_4^{2-}. Sulfide standards as per [98].	Dionex AG4A-SC and AS4A-SC in series	2.4 mM Na_2CO_3/2.2 mM $NaHCO_3$	Suppressed conductivity	0.75-1.1 µM	[149]
SO_3^{2-}, S^{2-}, $S_2O_3^{2-}$, S_x^{2-} (as S^{2-} and $S_2O_3^{2-}$)	Blast furnace slag leach solution	S_x^{2-} reacted to form S^{2-} and $S_2O_3^{2-}$ with SO_3^{2-} on-column.	Unknown anion-exchange resin	Two eluents (a) 0.5 M $NaNO_3$ followed by (b)100 mg/L SO_3^{2-}	Controlled potential coulometic	-	[150]
S^{2-}, SO_3^{2-}, SO_4^{2-}, $S_2O_3^{2-}$, S_x^{2-} (as S^{2-} and SCN^-)	Polysulfide solutions	Cyanolysis of polysulfide to S^{2-} and SCN^-.	TSKgel IC-Anion-PW	0.5:3:12:84.5 glycerin:*n*-Butanol:ACN:1.3 mM potassium gluconate, 1.3 mM boric acid, 1.3 mM sodium tetraborate (pH 8.5).	Suppressed conductivity, UV (220 nm)	4.9-68 µM	[151]

Table 1.1 (Cont.)

Species Detected	Sample	Sample Preparation	Column	Eluent	Detection	Detection Limit	Ref.
SO_3^{2-}, $S_2O_3^{2-}$, $S_4O_6^{2-}$	rDNA protein process solutions	Filtration	Hamilton PRP-X100 PS-DVB (10 µm particles) with Waters C18 Guard-PAK guard	10:90 ACN:H_2O with $NaClO_4$ gradient. ACN was not added if SO_3^{2-} not determined.	UV (214 nm)	30-50 µg/L (0.22-0.27 µM)	[152]
SO_3^{2-}, $S_2O_3^{2-}$, $S_4O_6^{2-}$	rDNA protein process solutions	Filtration	Alltech Universal Anion (10 µm particles) with Waters C18 Guard-PAK guard	10-150mM $NaClO_4$ gradient	UV (214 nm)	-	[152]
SO_4^{2-}, $S_2O_3^{2-}$, $S_2O_6^{2-}$	Hot spring water	-	Dionex HPIC-AG4A	0.2 mM phthalate eluent (pH 5.7)	Suppressed conductivity	1.8-15 µM	[153]
SO_4^{2-}, $S_2O_3^{2-}$, $S_2O_6^{2-}$	Standards	-	Hamilton PRPx100 PS-DVB with guard	0.5 mM 2,5-dihydroxy 1,4-benzenedisulfonic acid	Indirect UV (335 nm)	< 1 mg/L (<6 µM)	[154]
SO_4^{2-}, $S_2O_3^{2-}$, $S_3O_6^{2-}$, $S_4O_6^{2-}$	Standards	-	Shodex 524A PS-DVB	2.5 mM *p*-hydroxybenzoate (pH 9.7)	Non-suppressed conductivity	-	[155]
SO_4^{2-}, $S_2O_3^{2-}$, total $S_xO_6^{2-}$ x ≥ 4 as SCN^- and $S_2O_3^{2-}$.	Hydrothermal waters	$S_2O_3^{2-}$: 1 mL 1 M $ZnCl_2$, amber bottle. $S_xO_6^{2-}$: As above + 1 mL 1 M NaOH 1 mL 1 M KCN.	2 x Dionex AG4A guard columns in series. Dionex AS4A (SO_4^{2-} only)	$NaHCO_3/Na_2CO_3$ eluents	Suppressed Conductivity	0.1-0.5 µM	[156]
(a) $S_2O_3^{2-}$, total $S_4O_6^{2-}$, $S_5O_6^{2-}$, $S_6O_6^{2-}$ as SCN^-. (b) SO_3^{2-}, SO_4^{2-}	Standards	(a) Filtration, addition of cation-exchange resin, phosphate buffer (pH 7.4) added, cyanolysis. (b) Addition of formaldehyde and cation-exchange resin.	Dionex L-20 anion separator (a) 95 mm (b) 75 mm	(a) 3.0mM Na_2CO_3, 0.75mM *p*-cyanophenol (pH 11.8) (b) 0.75 mM Na_2CO_3, 0.75 mM *p*-cyanophenol (pH 11.4)	Suppressed conductivity	(a) 4.14-5.33 µM (b) 4.58-5.44 µM	[57]

Table 1.1 (Cont.)

Species Detected	Sample	Sample Preparation	Column	Eluent	Detection	Detection Limit	Ref.
(a) $S_2O_3^{2-}$, $S_3O_6^{2-}$, $S_4O_6^{2-}$, $S_5O_6^{2-}$ (b) SO_4^{2-}, $S_2O_3^{2-}$	Carbonate leaching solutions	-	Separon (a) HEMA 1000 epoxidized copolymer modified with DEtA (b) H300 DEAE in glass column	(a) 25 mM $NaClO_4$ and 5 mM phosphate buffer (pH 6.0) (b) 0.05 mM Sulfosalicylic acid (pH 6.0 with NaOH)	(a) UV (205 nm) (b) Indirect UV (254 nm)	(a) 0.6-3.3 mg/L (2.7-17 µM) (b) 8-40 mg/L (83-357 µM)	[157,158](a) only
$S_4O_6^{2-}$, $S_3O_6^{2-}$, $S_2O_3^{2-}$	Sediment slurries and enrichment cultures	Centrifugation and filtration	Sykam LCA A08 polymer coated silica based anion exchange	10:20:70 MeOH:H_2O:ACN containing 200 mM NaCl	UV (216 nm)	0.03-2 µM	[159]
$S_2O_3^{2-}$, $S_3O_6^{2-}$, $S_4O_6^{2-}$, $S_5O_6^{2-}$	Standards	-	Stainless steel column packed with 200 to 270 mesh Darco Red label activated carbon	Gradient (A) 0.5:99.5 THF:H_2O containing 11 g/L Na_2HPO_4 (adjusted to pH 10), (B) 50:50 THF:(A)	UV (254 nm)	3.7-360 mg/L (14 µM- 3.2 mM)	[160]
$S_2O_3^{2-}$, $S_3O_6^{2-}$, $S_4O_6^{2-}$, $S_5O_6^{2-}$	Mining wastewater and environmental samples	Extraction with $CHCl_3$ followed by analysis of diluted H_2O layer.	Dupont Permaphase AAX	Step gradient from 20 µM to 1.2 mM sodium citrate in H_2O	PCR, fluorescence	~0.3 mg/L (1.2-2.7 µM)	[161,162]
$S_2O_3^{2-}$, $S_3O_6^{2-}$/$S_4O_6^{2-}$, $S_5O_6^{2-}$, $S_6O_6^{2-}$	Standards	-	5 µm Applied Science SAX	1 mM sodium citrate (pH 5.0)	UV (218 nm) and off-line post-column polarography	-	[163]
$S_3O_6^{2-}$, $S_4O_6^{2-}$, $S_5O_6^{2-}$	Standards	-	Dionex HPIC-AG4A	5 mM phthalate eluent (pH 5.7)	Suppressed conductivity	8.7-36 µM	[153]
$S_3O_6^{2-}$, $S_4O_6^{2-}$, $S_5O_6^{2-}$, $S_6O_6^{2-}$	Coal plant process samples	Dilution	Glass column packed with VYDAC SAX resin. Guard used.	H_2O - 0.25 M $NaClO_4$, 0.1 M $NaBO_2$ (pH 2.5) gradient	PCR, UV (335 nm)	~20-40 µM	[131]

Table 1.2 Ion-interaction chromatographic methods for the determination of sulfur species.

Species Detected	Sample	Sample Preparation	Column	Eluent	Detection	Detection Limit	Ref.
S^{2-}, SO_3^{2-}, $S_2O_3^{2-}$	Standards	-	Chrompack cyano-bonded silica Sil 60-D 10-CN	40:60 MeOH-H_2O containing 0.1 M Na_2HPO_4/0.1 M KH_2PO_4/0.1% (*w/v*) CTABr	UV (215 nm)	~2 µM (S_2O_3)	[164]
SO_3^{2-}/SO_4^{2-}, $S_2O_3^{2-}$	Standards	-	Dionex MPIC-NS1	15:85 ACN-2 mM TBAOH/0.88 mM Na_2CO_3	Suppressed conductivity	-	[132]
SO_3^{2-}, $S_2O_3^{2-}$, S_x^{2-} (x = 2 to 4)	Petroleum production effluent	Derivatisation using DTNP	Alltech Absorbosphere HS C_{18} with Applied Biosystems Spheri-5 RP-18 guard 5µm particle size	50 mM $NaOOCCH_3$/7.5 mM $TBAHSO_4$ (pH 3.5 with HCl) –ACN gradient system	UV (320 nm)	~0.1 µM (S_x species not quantified)	[165,166]
S^{2-}, SO_3^{2-}, $S_2O_3^{2-}$, S_x^{2-}	Commercial sodium sulfide	Degassed water used	Hamilton PRP-1 5 µm particles or Polymer Labs. PLPR-S, 8 µm particles	15:85 *v/v* ACN-H_2O containing 1 mM Na_2CO_3 and 2 mM TBAOH (pH ~11)	UV (215 nm)	0.01-0.02 wt% (2-5 µM)	[167,168]
S^{2-}, $S_2O_3^{2-}$, $S_4O_6^{2-}$	Gold cyanide leach solutions	-	Dionex MPIC-NS1	23:2:75 *v/v* ACN:0.1M TBAOH in 2-PrOH/MeOH:H_2O containing 0.46mM Na_2CO_3/0.56 mM $NaHCO_3$	UV (240nm)	-	[169]
SO_4/SO_3^{2-}, $S_2O_6^{2-}$	Manganese leach solutions	Stabilisation of SO_3^{2-} with formaldehyde, dilution.	Dionex MPIC-NG1	20 wt% ACN-1 mM Na_2CO_3 and 2 mM TBAOH	Suppressed conductivity	-	[97]
SO_4^{2-}, $S_2O_3^{2-}$, $S_2O_6^{2-}$	Gold extract solutions	Dilution	Dionex MPIC-NG1 and NS1	10:90 ACN-H_2O containing 2.0 mM TBAOH and 2.0 mM Na_2CO_3	Suppressed conductivity	0.01-0.04 mg/L (89 nM-0.25 µM	[112,170]
SO_3^{2-}, SO_4^{2-}, $S_2O_3^{2-}$, $S_2O_6^{2-}$, $S_4O_6^{2-}$	Standards	-	Merck LiChrospher-100CH	14:86 ACN-1 mM TBAOH /7.5 mM H_3BO_3	Suppressed conductivity	10-70 µg/L (0.1-0.3 µM)	[132]
SO_4^{2-}, $S_2O_3^{2-}$, $S_2O_6^{2-}$, $S_4O_6^{2-}$	Standards	-	Superspher RP-18 4 µm particle size	4:96 *v/v* ACN- 0.3 mM TBAOH/20 mM H_3BO_3 (pH 7.9)	UV (215 nm) and suppressed conductivity	0.25-3 mg/L (3-13.4 µM)	[171]

Table 1.2 (Cont.)

Species Detected	Sample	Sample Preparation	Column	Eluent	Detection	Detection Limit	Ref.
(a) SO_4^{2-}, $S_2O_3^{2-}$, $S_2O_6^{2-}$, $S_3O_6^{2-}$ (b) SO_4^{2-}/$S_2O_3^{2-}$, $S_2O_6^{2-}$, $S_3O_6^{2-}$, $S_4O_6^{2-}$, $S_5O_6^{2-}$, $S_6O_6^{2-}$	Hot spring water	Dilution	Tokyo Kasei, Kaseisorb LC ODS super	(a) 10:90 or (b) 20:80 *v/v* ACN-H_2O containing 0.2 mM phthalate and 7 mM TPAOH (pH 5.0 with CH_3COOH)	Suppressed conductivity	0.03-0.29 mg/L (1.4-9.3 µM)	[172]
$SO_4/S_2O_3^{2-}$, $S_2O_6^{2-}$, $S_3O_6^{2-}$, $S_4O_6^{2-}$, $S_5O_6^{2-}$	Gold extract solutions	Dilution	Dionex MPIC-NG1 and NS1	26:74 ACN-H_2O containing 3.0 mM TBAOH and 2.0 mM Na_2CO_3	Suppressed conductivity	0.04-0.3 mg/L (0.25-1.3 µM)	[112,170]
$S_2O_3^{2-}$, $S_2O_6^{2-}$, $S_4O_6^{2-}$	Standards	-	Dionex MPIC-NG1 and NS1	20:80 ACN-2 mM TBAOH and 1 mM Na_2CO_3	Suppressed conductivity	-	[125]
$S_2O_3^{2-}$, $S_2O_6^{2-}$ /SO_4^{2-}, $S_3O_6^{2-}$, $S_4O_6^{2-}$, $S_5O_6^{2-}$	Standards	-	Hamilton PRP-1 reverse phase (PS-DVB) 10 µm particles	8:92 ACN-H_2O containing 5 mM TBABr	Non-suppressed conductivity	0.42-34 mg/L (2.55-133 µM)	[173]
$S_2O_3^{2-}$, $S_3O_6^{2-}$, $S_4O_6^{2-}$, $S_5O_6^{2-}$	Standards	-	Chrompack glass column containing CP SpherC_{18}	30:70 ACN-H_2O containing 1mM Na_2CO_3 and 2 mM $TBAH_2PO_4$ (pH ~7)	UV (215 nm)	-	[174]
$S_2O_3^{2-}$, $S_3O_6^{2-}$, $S_4O_6^{2-}$, $S_5O_6^{2-}$	Standards	-	Chrompack cyano-bonded silica Sil 60-D 10-CN	55:45 MeOH-H_2O containing 0.1 M Na_2HPO_4/0.1 M KH_2PO_4/0.1% (*w/v*) CTABr	UV (215 nm)	1.8-34 µM	[164]
$S_2O_3^{2-}$, $S_3O_6^{2-}$, $S_4O_6^{2-}$, $S_5O_6^{2-}$, $S_6O_6^{2-}$	Standards	-	Dionex MPIC-NS1	4:27:69 MeOH-ACN-H_2O containing 1 mM Na_2CO_3 and 2 mM TBAOH	UV (254 nm)	-	[174]
$S_2O_3^{2-}$, $S_3O_6^{2-}$, $S_4O_6^{2-}$, $S_5O_6^{2-}$, $S_6O_6^{2-}$	Hot spring waters	-	A Shinwa Ultoron VX ODS	20:80 *v/v* ACN-H_2O containing 6 mM TPAOH, (pH 5.0 with CH_3COOH)	UV (230 nm)	10-30 nM (not specified for $S_3O_6^{2-}$)	[175]
$S_2O_3^{2-}$, $S_3O_6^{2-}$, $S_4O_6^{2-}$, $S_5O_6^{2-}$, $S_6O_6^{2-}$	Dithionite or Rongalite ($HOCH_2SO_2^-$) standards	Derivatisation of dithionite to Rongalite	Polymer labs. PRLP-S 8 µm particles with Knauer PRP-100 guard	25:75 *v/v* ACN-H_2O containing 1 mM Na_2CO_3 and 2mM $TBAH_2PO_4$ (pH 7.7)	UV (215nm)	-	[168, 176,177]

Table 1.2 (Cont.)

Species Detected	Sample	Sample Preparation	Column	Eluent	Detection	Detection Limit	Ref.
$S_2O_3^{2-}$, $S_3O_6^{2-}$, $S_4O_6^{2-}$, $S_5O_6^{2-}$, $S_6O_6^{2-}$	Hot spring water	Refrigeration of standards. CO_3^{2-} to stabilise thiosulfate standard.	Tosoh TSK gel ODS-Ts 5 µm	20:80 ACN-H_2O 3mM TPAOH and 6 mM CH_3COOH (pH 5.0)	PCR with indirect UV at 350 nm	0.001-4.3 µM	[178]
$S_2O_3^{2-}$, $S_xO_3^{2-}$ (x = 3 to 11) (two separations required)	NS	-	Dionex IonPac NS1	ACN-H_2O containing TBAOH and Na_2CO_3	UV (254 nm)	-	[141]
$S_3O_6^{2-}$, $S_4O_6^{2-}$, $S_5O_6^{2-}$	Sea water	Pre-concentration, chloride minimisation	Hamilton PRP-1 (10 µm) with Brownlee PRP-1 guard cartridge	25:75 ACN:H_2O containing 10 mM Waters low-UV PIC-A/1 mM Na_2CO_3/1 mM $NaHCO_3$/30 mM NaCl/3 mM $NaClO_4$.	UV (205 nm)	~0.3-1 nM	[179]
$S_3O_6^{2-}$, $S_4O_6^{2-}$, $S_5O_6^{2-}$	Crater lake water	Removal of Cl^-, SO_4^{2-}, $S_2O_3^{2-}$	Showa Denko IC I-613 polystyrene gel	3.3:96.7 THF-H_2O containing 1 mM Phthalic acid 0.5 mM TBAOH (pH 3.5)	Non-suppressed conductivity	-	[61,180]
$S_xO_6^{2-}$, (x = 4 to 10)	Crater lake water	Addition of HAH, or exclusion of O_2 [61]. Refrigeration [181].	Spherisorb S30D2S ODS 3 µm	ACN-H_2O containing 0.1 M KH_2PO_4 + various concentrations of TBAOH to pH 3.5 with H_3PO_4.	UV (220 nm)	0.7-52 µM (quantitation limits, no value for $S_xO_6^{2-}$, x> 6)	[61,180,181]
$S_xO_6^{2-}$ (x = 4 to 18)	*Thiobacillus ferrooxidans* cultures	Centrifugation	Octadecylsilane (C18) Brand not specified	30:70 *v/v* ACN-H_2O with linear gradient of Na_2CO_3 (2 mM) and $TBAH_2PO_4$ (1 mM) to zero	UV (215 nm)	-	[182]
$S_xO_6^{2-}$ (x=5 to 11)	Reaction Mixture	-	Dionex MPIC-NS1	40:60 ACN-H_2O containing 1 mM Na_2CO_3 and 2 mM TBAOH	UV (254 nm)	-	[174]
$S_xO_6^{2-}$ (x = 5 to at least 32), S^0	Synthetic polythionate solutions	-	Keystone Scientific Partisil 5 µm ODS-3 reverse-phase	50:50 24 mM $TBAH_2PO_4$ (pH 3.6-4.0)-ACN. ACN gradients also used.	UV (254 nm)	-	[183]
$S_xO_6^{2-}$ (x = 9 to 22)	*Thiobacillus ferrooxidans* cultures	Centrifugation	Octadecylsilane (C18) Brand not specified	40:60 *v/v* ACN-H_2O with linear gradient of Na_2CO_3 and $TBAH_2PO_4$ (initially both 2 mM) to zero	UV (215 nm)	-	[182]

the analytes. For example, polythionate separations are easier to achieve using ion-interaction methods since retention on anion-exchange resins can be extremely high as the value of x in $S_xO_6^{2-}$ increases. Tables 1.1 and 1.2 list the anion-exchange and ion-interaction methods currently available for sulfur species analysis, with the separated analytes being listed in order of their elution. Some methods have additionally separated other anions, for example chloride, however only the relevant sulfur anions have been listed. Co-elution of analytes has been indicated by a '/' between the two relevant ions, whilst similar methods have been grouped together as one entry in the table. The information shown for a particular entry in the table refers to the first reference listed.

1.6.3.4 Resolution and Selectivity by Anion-Exchange and Ion-Interaction Chromatography

The separation selectivity of sulfur species in both anion-exchange and ion-interaction chromatography generally results in the following elution order:

$$S^{2-} \leq SO_3^{2-} \leq SO_4^{2-} \leq S_2O_3^{2-} \leq S_2O_6^{2-} \leq S_xO_6^{2-} \text{ (in order of increasing } x) \qquad (1.18)$$

The metallo-thiosulfates and polysulfides (S_x^{2-}) are not included in this list because the retention behaviour of these species has not been sufficiently characterised. The separation of polysulfides has been examined in a variety of papers [150,165,167], but with only limited success as will be discussed later, but they have been shown to be eluted after thiosulfate. No methods for the separation of the metallo-thiosulfates were identified, possibly due to there previously being no requirement to quantify these ions. Elemental sulfur, being both neutral and insoluble in water, has also been omitted from consideration since it is not amenable to determination by IC. However, Kupchella [183] has

noted that elemental sulfur could be eluted using ion-interaction chromatography in the presence of long chain length polythionates. This was explained in terms of micelle formation of the polythionates which enabled solubilisation of elemental sulfur.

Some variations to the selectivity order given in 1.18 have been reported. A Sykam LCA A08 polymer-coated silica-based anion-exchange column used with an eluent of 10:20:80 MeOH-H_2O-ACN containing 200 mM sodium chloride was able to separate thiosulfate, trithionate and tetrathionate in the reverse order to that given in Eqn. 1.18 [159]. The selectivity of this column was the same in a purely aqueous eluent containing 100 or 50 mM sodium chloride, however the use of a 5:60:35 MeOH:H_2O:ACN with 200 mM eluent gave an elution order of trithionate, thiosulfate and tetrathionate. Thiosulfate has been eluted prior to sulfite and sulfate using a mid-run column-switching technique, with thiosulfate passing through the guard column only before reaching the detector [104,139]. Story [131] and Ono [150] have both been able to alter the selectivity of sulfide, with the former study achieving elution of sulfide after thiosulfate, and the latter the elution of sulfide after sulfite, but no explanation was provided as to the reason for the change in selectivity. Story did note that on the VYDAC-SAX column, when used in the phosphate form, sulfite and sulfate were unretained. It has also been reported, again with no explanation, that sulfate can be eluted prior to sulfide using a carbonate eluent and an Oka-1 resin [148].

The difference in retention behaviour between the earliest (sulfide) and the latest (higher polythionates) eluted species is extremely large and has prevented any

separation of all sulfur species in one run. However, it is improbable that any sample would contain all the sulfur anions considered in this review because such a mixture would be unstable due to reactions between the various species [58]. Retention behaviour is the result of a number factors, particularly the charge on the analyte anion. This can be illustrated by the retention behaviour of sulfide, which in an alkaline eluent exists predominantly in the form HS^- (pK_{a2}=13.9 [184]) and in acidic eluents as non-ionic H_2S (pK_{a1} = 7.02 [184]). It therefore has a lower retention than the other more highly charged sulfur species. Sulfite exists as HSO_3^- (pK_{a2} = 7.18 [184]) in acidic eluent, which will reduce retention of this species, again on the basis of charge. Specific information on the separation mechanisms for the remaining sulfur ions is limited, although it is possible that hydrophobic interactions could form a significant role for the polythionates as the value of x in $S_xO_6^{2-}$ increases. A general discussion of factors that determine ion-exchange selectivity can be found elsewhere [113].

Separations of sulfur anions generally fall into one of two main categories - those containing some or all of the less strongly retained species (sulfide, sulfite, sulfate and thiosulfate) and those of thiosulfate and the polythionates. Dithionate separations usually include sulfate and/or thiosulfate and occasionally polythionates as additional analytes. Different chromatographic techniques are preferred for the separation of each of the two main groups. While sulfide, thiosulfate, sulfate and sulfite have been determined by both anion-exchange and ion-interaction chromatography, they are most commonly chromatographed using the former technique. The generally stronger retention observed with anion-exchange resins is more suited to the separation of these comparatively weakly

retained ions. On the other hand, ion-interaction techniques have found more frequent application to the separation of the polythionates due to the generally weaker analyte-stationary phase interactions possible with this separation method when compared with anion-exchange resins. There does not appear to be any literature reference to the use of IC for the separation of higher polythionates ($S_xO_6^{2-}$, x >6), other than by ion-interaction techniques.

There are many methods in Tables 1.1 and 1.2 used to separate three of four ions from sulfide, sulfite, sulfate and thiosulfate, but only a few determine all four simultaneously [101,107,142,143,147,148,151]. Even fewer of these actually provide a chromatogram to allow assessment of the resolution between the various peak pairs. In some cases multiple detectors [143,148,151] were used in order to enable detection of all four species. Divjak and Goessler [147] were able to separate these four sulfur anions in ~17.5 min on a Dionex AS12A column with AG12A guard using a sodium hydroxide step gradient. The success of the separation was dependent on the use of the element-specific MS detector since chloride was co-eluted with sulfide, which would cause problems if a universal detection method, such as conductivity, was used.

An alternative technique for sulfite, sulfate and thiosulfate sulfide (and thiocyanate) determination was recently described by Jekakumar *et al.* [149], using a Dionex AS4A-SC column with carbonate/bicarbonate eluent and suppressed conductivity. In this method sulfide was determined indirectly by injecting two aliquots of each sample, one of which had been treated with an ammoniacal peroxide solution to convert all the sulfur species present to sulfate.

From the untreated solution the equivalent sulfate concentration of all the sulfur anions under direct investigation was calculated and compared with the treated solution to determine the sulfide by difference. However, this method is only applicable in the absence of further sulfur compounds.

Separation of thiosulfate and the lower polythionates (x = 3 to 6) has been achieved by a number of authors, as is apparent in Table 1.2. Those using UV detection clearly demonstrate the relatively poor detection limits attainable for trithionate by this methodology. Kupchella [183] obtained good resolution of the polythionates $S_5O_6^{2-}$ to $S_{32}O_6^{2-}$ in 46 min on a Keystone scientific Partisil 5 μm ODS-3 column with a gradient between (A) a solution of 24 mM $TBAH_2PO_4$ (pH 4) and (B) ACN. This represents the most comprehensive polythionate separation reported to date.

The determination of polysulfides by IC has been problematic [127,150,151,165,167] with accurate results and adequate separation being difficult to obtain. Uddin *et al.* [127] concluded that with their anion-exchange method polysulfides broke down to sulfide and elemental sulfur on the column. Other anion-exchangé methods have involved derivatisation of the polysulfides, either prior to the separation using cyanolysis to form thiocyanate and sulfide [151] or during the separation using sulfitolysis to form thiosulfate and sulfide [150]. Ion-interaction HPLC techniques have been the most successful for direct separation of polysulfides [167] from other sulfur anions, but even here only a single peak for the unresolved polysulfides was observed. The inability of such methods to separate individual polysulfides is caused by the rapid equilibria

existing between the different members of the series. Witter *et al.* [165] has provided the best separation of polysulfide species and in this study derivatisation of thiosulfate and sulfite was achieved with 2,2'-dithiobis(5-nitropyridine) (DTNP). In the subsequent chromatographic separation, peaks were observed in the chromatogram that were attributable to derivatives of a 90% S_4^{2-} sample known to be contaminated with other polysulfides.

Reports on the separation of sulfur species with non-commercial columns are few. Chapman and Beard [160], used a column packed with activated carbon to separate thiosulfate and the polythionates. Baseline resolution was not achieved between the thiosulfate-trithionate and tetrathionate-pentathionate peak pairs. No subsequent papers have appeared using this technique, a possible reason given by Story [131] being that it is difficult to prepare reproducible columns. Vlacil and Vins [157,158], functionalised Separon hydroxyethyl methacrylate (HEMA) epoxidised copolymers with diethanolamino groups and used the resin to resolve thiosulfate and polythionates ($x = 3$ to 5). The separations obtained in both papers can be bettered on commercial resin materials, as can be seen in Tables 1.1 and 1.2.

1.6.3.5 Sulfur Ion Detection in Ion-Chromatography

A broad range of detection techniques has been used in conjunction with the IC methods, with by far the most popular being UV spectrophotometry and conductivity. Most of the sulfur species covered in this review have at least some absorbance in the UV region 200-254 nm, with the main exceptions being sulfate and dithionate [113,185]. Trithionate absorbs relatively weakly compared with the other polythionates [186] and as a result detection limits for this ion using UV

detection are relatively high, as noted by a number of workers [159,160,164,175]. Indirect UV detection has been used as an alternative for separations of non-UV absorbing analyte anions, such as sulfate [94,130,154,157].

Conductivity detection in both the suppressed and non-suppressed forms has also found wide application (see Tables 1 and 2). This technique is more universal than direct UV detection and while this means that it can detect all ionic sulfur species, it will also detect any interfering ions in the sample matrix. Sulfide cannot be determined sensitively and reliably in suppressed systems since the suppressor converts this ion to the non-conductive species H_2S [102,113,187].

Of the electrochemical detection techniques other than conductivity, the most frequently reported have been DC and pulsed amperometry for detection of sulfide, sulfite and/or thiosulfate [102,125,128,140,142]. The electro-inactive sulfate ion has also been determined by indirect amperometry in a suppressed IC system [142], where the detection electrode was used to measure the change in eluent pH that occurred with the elution of strong acid anions in suppressed IC [113]. In some papers [102,125] a dual detection system was used incorporating amperometry and conductivity in order to improve the detection limits of ions such as sulfide and thiosulfate. Amperometry has the problem of electrode poisoning, as noticed in the detection of sulfide by Poulson and Borg [101] using DC amperometry with a silver electrode. These authors postulated that organic materials in the samples fouled the detection electrode. A gradual increase in the signal for sulfide from a clean silver electrode over the first few injections prior to attaining consistent results has also been reported [102]. This effect has been attributed to the formation of a layer of silver sulfide on the electrode, enhancing

the electrode reaction. The layer also enhanced the detection of other sulfur species, notably thiosulfate and sulfite.

Literature also exists for techniques involving polarographic detection. Sulfide, sulfite and thiosulfate have been detected using sampled DC polarography [127] and a method has been developed for thiosulfate and the polythionates ($x = 3$ to 6) [163] where fractions of the column effluent were collected and analysed polarographically. The chromatographic method was unable to separate tri- and tetrathionates, and the concentrations of these could only be determined through calculation after the polarographic experiments were completed. No detection limits were specified in either case.

Inductively coupled plasma-mass spectrometry (ICP-MS) has recently been demonstrated as a further detection method for sulfur species [147]. A suppressed IC method developed using this detector has been applied to the separation of sulfide, sulfite, sulfate, and thiosulfate using a NaOH eluent, with detection of these ions being effected as $^{32}S^{16}O^{+}$ $m/z = 48$. This particular species was chosen due to high background at the two main sulfur isotope m/z ratios of 32 and 34. Carbonate eluents could not be used since carbon suppressed the ICP-MS signal for $^{32}S^{16}O^{+}$ and chemical suppression of the eluent was also required to remove sodium ions which would otherwise salt out and block the detector interface. Separation of matrix ions from the sulfur species of interest is usually not required, but high concentrations of ions such as chloride that are co-eluted with sulfide under the chromatographic conditions used will suppress the signal obtained for sulfide. Detection limits were between 35-270 μg/L (1.1-2.5 μM)

which, although being low, are still about an order of magnitude higher than for some suppressed conductivity, UV and post-column reaction (PCR) methods. However, an advantage of ICP-MS is its selectivity for sulfur species.

Wolkoff and Larose [161,162] employed a PCR system whereby the polythionates (x = 3 to 6) were reacted with hydroxide to form thiosulfate and sulfite. These products were oxidised with cerium(IV) to produce cerium(III) through the following reactions:

$$S_2O_3^{2-} + 8Ce^{4+} + 5H_2O \longrightarrow 2SO_4^{2-} + 8Ce^{3+} + 10H^+ \quad (1.19)$$

$$SO_3^{2-} + 2Ce^{4+} + H_2O \longrightarrow SO_4^{2-} + 2H^+ + 2Ce^{3+} \quad (1.20)$$

The cerium(III) generated in this way was then detected using fluorimetry. Problems with the technique were that the reactions respond to any oxidisable material in the sample, leading to possible interferences, and there was no response to sulfate. The procedure outlined in this paper has become somewhat outdated, in that similar or improved detection limits have been reported for methods utilising suppressed conductivity detection [112,172]. A new method using the technique has recently appeared for sulfite and thiosulfate [188] and demonstrates sub-μM detection limits. Story [131] developed a method that utilised bromine to convert sulfide, sulfite, thiosulfate and the polythionates (x = 3 to 6) to sulfate. The reaction for thiosulfate is:

$$5H_2O + 4Br_2 + S_2O_3^{2-} \longrightarrow 8Br^- + SO_4^{2-} + 10H^+ \quad (1.21)$$

The resultant sulfate was detected as $Fe(SO_4)^+$ by UV spectroscopy at 335 nm after the introduction of iron(III). This is the most universal PCR system that has

been developed for sulfur species and has detection limits in the range 20-100 μM, showing that it is less sensitive than many of the other detection methods available.

PCR detection systems that determine a small number of sulfur anions also exist. Sulfide, thiosulfate and the polythionates ($S_xO_6^{2-}$, $3 \leq x \leq 6$) have all been determined through their ability to catalyse the reaction of iodine with azide

$$2N_3^- + I_2 \longrightarrow 3N_2 + 2I^- \qquad (1.22)$$

This PCR was followed by indirect detection of the excess iodine as tri-iodide at 350 nm [98,178]. An alternative method has used a similar approach for sulfide, sulfite and thiosulfate, except in this case the catalysed reaction was the degradation of potassium bromate in hydrochloric acid, with detection at 522 nm [148]. Other methods [96,98] have used the following iodometric reactions as the basis for a PCR system to detect sulfide, sulfite and thiosulfate

$$2S_2O_3^{2-} + I_2 \longrightarrow S_4O_6^{2-} + 2I^- \qquad (1.23)$$

$$S_2^{2-} + I_2 \longrightarrow S^0 + 2I^- \qquad (1.24)$$

$$SO_3^{2-} + I_2 + H_2O \longrightarrow SO_4^{2-} + 2I^- + 2H^+ \qquad (1.25)$$

The iodine was stabilised in solution as the tri-iodide ion and detection was achieved by measuring the reduction in the absorbance of tri-iodide. All of the above techniques provide very low (sub μM) detection limits, particularly those involving catalysis.

1.6.3.6 Pre-Chromatographic Derivatization and Preconcentration

Pre-analysis derivatization of sulfur anions has been used to obtain low detection limits and to prevent degradation of these ions prior to analysis. The compound

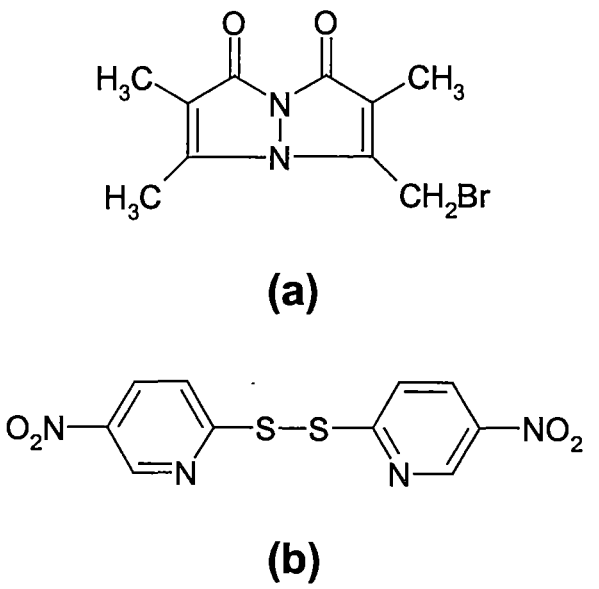

Fig. 1.3 Chemical structures of **(a)** monobromobimane **(b)** DTNP.

2-2'-dithiobis(5-nitropyridine) (DTNP), illustrated in Fig. 1.3(a), is a typical derivatisation reagent which has been used for the determination of thiosulfate and sulfite [165,166], after conversion, via a displacement reaction, to disulfide derivatives. A by-product of the reaction is 2-mercapto-5-nitropyridine. The reagent also reacts with polysulfide species but quantitative detection was not possible because of a lack of standards for identification of individual polysulfides. Detection limits in the mid-nM range were attained in conjunction with preconcentration of the derivatives on Sep-Pak C_{18} cartridges. The derivatives were found to be stable on the cartridges for two weeks if kept refrigerated at <5°C. The technique has been applied to seawater [166] and effluent from petroleum production [165]. One problem with the method was that derivatisation was found to perturb sulfur speciation [165], since results by this method were on average 33% higher than those observed for the same samples using differential pulse polarography.

A second derivatization reagent, monobromobimane (MBB, shown in Fig. 1.3(b)) has been applied to sample matrices such as human serum [126] for the determination of sulfide, sulfite and thiosulfate, through their conversion to fluorescent derivatives formed by displacement of bromide in the molecule by the sulfur containing ion. These derivatives have also been separated using reverse phase HPLC [189-192]. No substantial comparative studies have been conducted with this reagent so possible perturbation effects on the equilibrium speciation of sulfur caused by pre-treatment are unknown. The bimane derivatives formed from seawater samples were found to be stable for several months if kept frozen at

-20°C [190]. Detection limits in the mid-nM range were achieved with this system.

Preconcentration of the polythionates (x = 3 to 5) on a Waters IC-PAK anion-exchange pre-column followed by separation by ion-interaction chromatography on a Hamilton reversed phase column was reported by Weir *et al.* [179]. Using this technique extremely low detection limits for these ions of between ~0.3-1 nM were attainable (0.08 –0.2 μg/L). One problem with the preconcentration method was that under the conditions required for elution from the pre-column and separation, thiosulfate was eluted with the solvent front and therefore could not be determined accurately.

1.6.4 Determination of Sulfur Species using Capillary Electrophoresis

1.6.4.1 Introduction [193,194]

CE is an electromigrative separation technique in which the separation mechanism is effected by the differing rates of migration (electrophoretic mobilities) of the analyte ions in an electric field. In this technique separations are carried out in a narrow bore capillary (I.D. typically 20-100 μm O.D. 375 μm) usually made of fused-silica coated with polyimide, the latter used to overcome the fragile nature of the silica. A CE instrument configuration is shown Fig. 1.4. The capillary is filled with, and each end immersed in, an ionic-solution at the desired pH known as the "background electrolyte (BGE)". An electrode from a high-voltage power supply is also placed in each of the electrolyte reservoirs. Samples are injected into the capillary by replacing the inlet electrolyte reservoir for a time with the

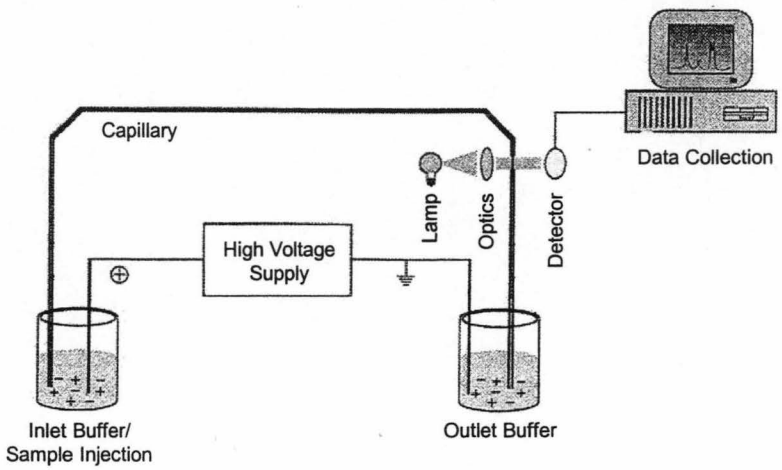

Fig. 1.4 Diagram of a typical capillary-electrophoretic system. Adapted from [194].

sample solution. Injection is usually facilitated by the use of hydrodynamic (a difference in height between the inlet and outlet of the capillary), pressure driven, or electrokinetic (applied voltage) means. After this process is completed, the inlet BGE is returned and separation is effected by applying a high voltage across the capillary, typically up to ±30 kV. This limits the size of the capillary that can be used since otherwise the heating, known as Joule heating, generated by the flow of a current in a conducting medium, would not be adequately dissipated and the liquid would boil. On application of the voltage the ions then separate according to differences in their electrophoretic mobilities. Near the outlet of the capillary, detection is effected, most commonly through the use of UV spectrophotometry. Which ions migrate towards the detector in a CE analysis depends on the polarity of the applied voltage, the effective mobility of the ions under investigation, and also the strength of the electro-osmotic flow (EOF). EOF is a phenomenon caused by the negative charge of ionised silanol groups on the wall of the fused-silica capillary, which results in the formation of an electrical double layer. That closest to the stationary silanol groups is essentially immobile (Stern Layer), however the adjacent, more diffuse zone (Outer Helmholtz Plane), is not. Under an electric field the cations in this second zone migrate towards the cathode, along with their waters of hydration. The hydrogen-bonding properties of water cause this effect to continue on to the bulk solution in the capillary, with the result that the entire electrolyte solution being drawn towards the cathode. As a result the observed mobility of an ion in a CE system is the vector sum of the electrophoretic mobility of the ion, and the EOF that exists in the capillary. EOF is dependent on a number of factors, notably pH, and can also be influenced or reversed by the use of various modifiers in capillary pre-flushing solutions and/or the electrolyte.

The advantages of CE over IC are that it gives faster, more efficient separations, while the disadvantages are that the technique is not as robust, reproducible and generally shows higher limits of detection.

1.6.4.2 Separation and Selectivity for Sulfur Anions by Capillary Electrophoresis

CE is a less developed technique in comparison to IC for the analysis of inorganic ions [195] but there have been many separations reported that include one or two sulfur anions [196]. These will not be covered here, as further information can be obtained in the review by Kaniansky *et al.* [196]. Table 1.3 outlines the separation of sulfur species that have been performed using CE. Some of the methods shown have also included the separation of other anions but only the relevant sulfur anions have been listed. As with the chromatography tables, co-elution of analytes has been indicated by a '/' between the two relevant ions and similar methods have been grouped together as one entry. The information shown for a particular entry again refers to the first reference listed. Analytes are listed in migration order.

Most research into the separation of sulfur anions by CE has focused on sulfide, thiosulfate, sulfite and sulfate, with separation generally being achieved with co-electro-osmotic flow (EOF) through the addition of an EOF modifier to the background electrolyte (BGE). In this separation mode the migration order is generally:

$$S_2O_3^{2-} \leq SO_4^{2-} \leq S^{2-} \leq SO_3^{2-} \quad (1.26)$$

Separations of other sulfur anions are too few in number to warrant inclusion of their migration order in the above series, although the two papers that have

Table 1.3 Capillary electrophoretic methods for the determination of sulfur species.

Species Detected	Sample	Sample Preparation	Electrolyte composition (pH, voltage applied)	Detection	Detection Limits	Ref.
$S_2O_3^{2-}$, S^{2-}, SO_3^{2-}	Standards	-	0.1 M Tris/HCl buffer (pH 8.75, -7 kV)	UV (200 nm)	-	[197]
$S_2O_3^{2-}$, S^{2-}, SO_3^{2-}	Photographic waste solutions	Dilution. On-capillary reaction with I_2 to form I^-. SO_3^{2-} standards in O_2 free water, S^{2-} standards by [98].	20 mM tris-HCl (pH 8.5, -30 kV)	Direct UV (214 nm) of iodide formed from derivatisation.	0.5-2 µM	[198]
(a) $S_2O_3^{2-}$, SO_3^{2-}, S^{2-} (b) $S_2O_3^{2-}$, S^{2-}, SO_3^{2-}	Stainless steel corrosion solutions	(a) used for high Cl^- samples, (b) used for high SO_4^{2-} samples.	(a) 25 mM NaCl, 4 mM Waters OFM Anion-BT in OH form (-20 kV) (b) 1.5 mM Na_2SO_4, 2 mM OFM Anion BT in OH form (pH 10.5, -20 kV)	Direct UV (214 nm)	-	[199]
$S_2O_3^{2-}$, SO_4^{2-}, SO_3^{2-}	Standards	Formaldehyde to stabilise SO_3^{2-}, and degassed water to stabilise S^{2-} standards	5 mM Na_2CrO_4, 20 µM CTABr (pH 10, -20 kV)	Indirect and direct UV (214, 254 nm)	0.17-0.50 mg/L (1.5-6.2 µM)	[99]
$S_2O_3^{2-}$, SO_4^{2-}, SO_3^{2-}	Standards, studying oxidation of SO_3^{2-}	5% PrOH added as stabiliser for SO_3^{2-}.	9.5 mM $K_2Cr_2O_7$, 1 mM DETA, 5 % *v/v* PrOH (pH 10.3, -25 kV).	Indirect UV (254 nm)	3-7 µM	[103]
$S_2O_3^{2-}$, SO_4^{2-}, S^{2-}/SO_3^{2-}	Standards	On-line dialysis	6 mM Na_2CrO_4, 32 µM CTABr, 3 mM H_3BO_3 adjusted to (pH 8.0, -25 kV)	Indirect UV (372 nm)	-	[200]
$S_2O_3^{2-}$, S^{2-}, SO_4^{2-}, SO_3^{2-}	Kraft black liquor	Dilution with degassed water	32:68 ACN:5 mM chromate, 0.001% HDB *w/v* (pH 10.8, -30 kV)	Indirect UV (185 nm)	0.5-1 mg/L (5-31 µM)	[62]
$S_2O_3^{2-}$, SO_4^{2-}, S^{2-}, SO_3^{2-}	Kraft process liquors	Dilution	5 mM Na_2CrO_4, 3.45 µM H_2SO_4, 0.5 mM Waters NICE-Pak OFM Anion-BT (-20 kV)	Direct and indirect UV (185, 214 or 254 nm)	-	[201]
$S_2O_3^{2-}$, SO_4^{2-}, S^{2-}, SO_3^{2-}	Kraft process liquors	On-line dilution	3.5 mM K_2CrO_4, 30 µM CTABr (pH 11, -25 kV)	Indirect UV (372 nm)	-	[202]
$S_2O_3^{2-}$, SO_4^{2-}, S^{2-}, SO_3^{2-}	Open-pit mining lake water	Filtration., formaldehyde to stabilise SO_3^{2-}, and degassed water to stabilise S^{2-} standards	50 mM CHES, 35 mM LiOH, 0.03% Triton X-100, pre injection rinse of 1 mM CTABr (-25 kV)	Conductivity	8-50 µg/L (83 nM-1.6 µM)	[99]
$S_2O_3^{2-}$, SO_4^{2-}, S^{2-}, SO_3^{2-}	Kraft process liquors	Dilution	5 mM Na_2CrO_4, 0.5 mM Waters Nice-Pak OFM Anion-BT (pH 10.6, -20 kV)	Indirect and direct UV (214, 254 nm)	-	[203]

TABLE 1.3 (Cont.)

Species Detected	Sample	Sample Preparation	Electrolyte composition (pH, voltage applied)	Detection	Detection Limits	Ref.
$S_2O_3^{2-}$, SO_4^{2-}, S^{2-}, SO_3^{2-}	Kraft process liquors	Dilution and helium degassing.	2.25 mM PMA, 6.5 mM NaOH, 0.75 mM hexamethonium hydroxide, 1.6 mM TrEA (pH 11.2, -18 kV)	PDA (350/50 nm)	~1 mg/L (9-31 µM)	[204]
$S_2O_3^{2-}$, SO_4^{2-}, S^{2-}, SO_3^{2-}	Kraft process liquors	Dilution with NaOH (pH 11) and degassing	20:80 ACN:5 mM Na_2CrO_4, 0.001% *w/v* HDB (pH 11.0, -15 kV).	Direct and indirect UV (185, 214, 254 nm)	-	[205,206]
$S_2O_3^{2-}$, SO_4^{2-}, S^{2-}, SO_3^{2-}	Standards, beverages and vinegar	-	6 mM K_2CrO_4, 3 mM boric acid, 23 µM of CTABr (pH 8.75, -25 kV)	Indirect UV (372 nm)	-	[207]
$S_2O_6^{2-}$, $S_2O_3^{2-}$, SO_4^{2-}	Standards	-	2.5 mM PMA, 6.5 mM NaOH , 0.75 mM hexamethonium hydroxide, 1.6 mM TrEA (pH 7.7, -30 kV)	Indirect UV (250 nm)	-	[208]
$S_2O_3^{2-}$, SO_4^{2-}, $S_2O_6^{2-}$, $S_4O_6^{2-}$	Standards	-	3 mM NTS, 2 mM DETA, 100 mM H_3BO_3, 5 mM $Na_2B_4O_7$ (pH 8, -30 kV)	Indirect UV (284 nm)	~80 µg/L for SO_4^{2-} (0.8 µM)	[209]
$S_2O_3^{2-}$, SO_4^{2-}, $S_4O_6^{2-}$ (injected separately), S^{2-}	Natural clayey water	-	10 mM TRIS, 1.5 mM PMA, 0.5 mM DETA (pH 8, -20 kV)	Indirect UV (214 nm)	3-20 µM	[64]
$S_2O_3^{2-}$, SO_4^{2-}, SO_3^{2-}, $S_4O_6^{2-}$	Photographic waste solutions	Dilution	5 mM H_2CrO_4, 1 mM hexamethonium hydroxide (pH 8.0 with TrEA, -30kV)	Indirect UV (254 nm)	0.8-8.4 µM (Not specified for $S_4O_6^{2-}$)	[210]
$S_2O_3^{2-}$, SO_4^{2-}, $S_3O_6^{2-}$, SO_3^{2-}, $S_4O_6^{2-}$, S^{2-}	Standards for salt purity and solutions studying reaction of SO_3^{2-} with $S_4O_6^{2-}$.		2 mM sulfosalicylic acid-0.5 Waters OFM-OH (pH 7.0 with bis-tris, -25 kV)	Indirect UV (214 nm)	1.5-10 µM	[211]
$S_2O_3^{2-}$, $S_4O_6^{2-}$, $S_5O_6^{2-}$, $S_6O_6^{2-}$	Thiosulfate electrolytic oxidation solutions	Dilution	5 mM KH_2PO_4, 5 mM $(NH_4)_2SO_4$ (pH 5.0, -30 kV)	Direct UV (214 nm)	0.8-8.4 µM	[210]
$S_2O_3^{2-}$, $S_4O_6^{2-}$, $S_5O_6^{2-}$, $S_6O_6^{2-}$	Photographic waste solutions	Dilution	5 mM TBAAc, 5 mM $(NH_4)_2SO_4$ (pH 5.0, -30 kV)	Direct UV (214 nm)	0.8-8.4 µM	[210]

considered polythionates [210,211] suggest that these ions migrate in order of increasing sulfur number with trithionate slower than sulfate. Deviations from the order given above have been reported with the most notable being sulfide migrating more slowly than sulfite [199] and sulfide migrating between thiosulfate and sulfate [62]. In the former case the change in selectivity was achieved through increasing the EOF modifier (OFM anion-BT (hexamethonium)) in the BGE from 2 mM to 4 mM. The change was attributed to a relatively strong reduction in sulfide mobility caused by the hydrophobicity of the ion and the formation of ion-pairs between sulfide and the EOF modifier. These ion-pairs could be formed with free modifier ions and/or micelles that form at this concentration. The faster migration of sulfide over sulfate was achieved by adding acetonitrile to the electrolyte [62]. This addition reduced the mobility of all the anions investigated, but the rate of decrease with increasing percentage of acetonitrile (ACN) was higher for sulfate than sulfide, resulting in a change in separation selectivity when the electrolyte contained ≥25% *v/v* ACN. These changes were attributed to solvation effects and to a lesser extent also to changes in the pH of the BGE caused by addition of the organic solvent.

The work in the literature to date demonstrates two advantages of CE over IC, these being shorter analysis times and greater separation efficiency [195]. This is highlighted by the research of Volgger *et al.* [62] who reported separations of thiosulfate, sulfate, sulfide, sulfite and other ions in less than 1 min in Kraft pulping liquors.

Separations including dithionate [208,209], trithionate [211] and/or tetrathionate [64,209-211] have been reported. In one case [64] tetrathionate had to be injected separately since precipitation occurred on mixing with the other three sulfur anions being examined (thiosulfate, sulfate and sulfide), probably through the sulfidolysis reaction (1.15). There are only two publications on the determination of thiosulfate and multiple polythionate ions [210,211]. The first examined thiosulfate and polythionates (x = 4 to 6) in photographic waste solutions, using direct UV detection. The BGE in this case consisted of 5 mM tetrabutylammonium (TBA) acetate and 5 mM ammonium sulfate at pH 5. Migration occurred in order of increasing sulfur number. In developing the separation method, it was found that the EOF modifier, tetradecyltrimethylammonium hydroxide (TTAOH), caused peak broadening of the polythionates, while a second modifier, hexamethonium hydroxide caused a broad hexathionate peak, both presumably due to ion-pair formation. As a result, the two BGEs developed in this work contained either no EOF modifier or a modifier of relatively low hydrophobicity (TBAOH), which was used to increase resolution between thiosulfate and bromide. Separation in both cases was counter-EOF, which had no significant effect on the separation since the EOF mobility was very low at the pH used. The second paper [211] employed indirect UV detection at 214 nm with an electrolyte containing 2 mM sulfosalicylic acid and 0.5 mM Waters OFM-OH EOF modifier, adjusted to pH 7.00 with bis-tris, and was able to separate sulfide, sulfite, sulfate, thiosulfate, trithionate and tetrathionate (and peroxodisulfate, $S_2O_8^{2-}$). It is the most comprehensive method for sulfur anions to date and the only one to have considered the trithionate ion by

CE. There are no CE separations in the literature to date which include, the higher polythionates (x >6), the polysulfides or the metallo-thiosulfates.

1.6.4.3 Sample Preparation, Preconcentration and Injection

Kuban and Karlberg [200,202,207] have developed coupled flow injection analysis FIA-CE systems designed to reduce or remove the need for off-line sample pre-treatment and to enable automated analysis. These FIA-CE systems have been used to dilute Kraft process liquor samples on-line prior to the CE separation of thiosulfate, sulfate, sulfide and sulfite [202] and also for on-line dialysis [200] and gas diffusion [207] pre-treatment methods. A range of anions were examined including sulfate, sulfide, thiosulfate and sulfite. Dialysis transport efficiencies were found to be quite low for the sulfur anions, ranging from between 7-10%, which reduced the analytical sensitivity for these ions. The gas dialysis process was only suitable for sulfide and sulfite since thiosulfate decomposed to give sulfur dioxide (which interfered in the quantification of sulfite) and elemental sulfur (which fouled the gas/liquid separation membrane).

Electrokinetic injection has been used to enhance the analytical sensitivity for thiosulfate, sulfate, sulfite sulfide and thiocyanate [99]. This process reduced detection limits for these ions to sub-μM levels, representing at least a twenty-fold improvement over standard hydrodynamic injection, giving some of the lowest detection limits observed in sulfur speciation studies by CE. The major problem with this approach (which occurs with any electrokinetic injection method) was a strong dependence of peak areas on sample composition, especially for highly conductive samples which gave low enrichment factors. External calibration curves were also non-linear as a result of this conductivity dependence, so

standard addition methods were suggested as an alternative method for quantifying analytes. However, care needed to be taken to ensure the standard addition did not significantly affect the conductivity of the sample. For further information on the advantages and disadvantages of electrokinetic injection readers are referred to a recent review by Krivacsy *et al.* [212]. Other reports have utilised electrokinetic injection for the determination of sulfur species [197,200,202,207] although no mention was made of detection limits, linearity or the dependence of sample conductivity on the amount of sample injected.

1.6.4.4 Detection of Sulfur Anions

Indirect UV detection is the most commonly used technique in CE for the detection of sulfur species, as is the case for most inorganic anions [196], although direct and mixed indirect/direct detection have also been used. The primary reason for the popularity of indirect UV detection is that many inorganic anions, such as sulfate, show little direct UV absorbance. The most common indirect detection "probe" (i.e. the UV-absorbing co-anion used to visualise analyte anions) employed in sulfur speciation studies has been chromate (see Table 1.3). Indirect detection can be problematic if some of the analytes absorb at the detection wavelength, leading either to reduced detection sensitivity or even complete failure to detect some analytes, as was observed by Padarauskas *et al.* for penta- and hexathionate at 254 nm using chromate or Tiron as the probe [210]. CE with conductivity detection was recently used for the determination of thiosulfate, sulfate, sulfide and sulfite [99], although detection limits when hydrodynamic injection was used were generally higher than for UV detection techniques.

Recently, a novel in-capillary derivatisation method was reported for the determination of thiosulfate, sulfide and sulfite [198]. In this technique a plug of an iodine solution was injected at the detection end of the capillary immediately prior to the start of the analysis. On application of the separation voltage the analyte ions migrated towards the anode, while the non-ionic iodine solution migrated towards the cathode with the EOF. During the analysis the iodine zone passed through each of the analyte zones, reacting to form iodide as one of the products. The generated iodide was then detected by direct UV at 214 nm. The main advantages of the method were that it improved the separation efficiency and shortened the analysis time. The authors also note that such an approach could be used for the simultaneous separation of UV and non-UV absorbing anions in a single run with direct UV detection.

One of the main disadvantages of CE for inorganic ions are the limited number of detection methods available, and relatively poor detection limits in comparison with IC [195]. CE with UV detection for sulfur speciation is no exception, with minimum detection limits achieved being approximately 1-10 μM for most ions. Only the use of electrokinetic injection as a preconcentration tool has enabled lower detection limits of sulfur ions by CE [99]. IC methods that attain significantly lower detection limits are available and these can also be used for a wider variety of sulfur anions than CE, as indicated in Tables 1.1 and 1.2.

1.6.5 Determination of Sulfur Species by Isotachophoresis

1.6.5.1 Introduction [213,214]

Like CE, capillary isotachophoresis (ITP), is an electromigrative technique, and therefore also uses the differing electrophoretic mobilities of ions as a means of

their separation. ITP is actually an older technique for the determination of ionic species than CE. The apparatus required is similar to CE (a standard CE instrument can be used), however there are a large number of differences between the two methods. Unlike CE, the use of much wider capillaries is possible, as is the use of segmented capillaries with different internal diameters. The wider bore capillaries also make possible the use of chromatographic-type injection valves. The electrolyte system used is discontinuous, with the buffer used initially to fill the capillary or "leading electrolyte" different to that used after injection, known as the "terminating electrolyte". In the case of anion separations, the leading electrolyte contains an anion of mobility higher than those of the analytes of interest in the sample, while the terminating electrolyte contains an anion of lower mobility than those in the sample. Unlike CE universal detectors such as conductivity are more commonly used than UV.

Separation of ions in isotachophoresis is based on the "regulating function" first described by Kohlrausch, which bears his name. The value of the function is independent of time and at a given point in the migration path is dependent only on what ions are present in the capillary prior to the application of the electric current. For strong, monovalent electrolytes, and assumptions of negligible diffusion and constant ionic mobilities, once a current is applied the function can, for any given point in the capillary, be expressed as shown in Eqn 1.27.

$$\sum \frac{c_i - c_i^0}{|u_i|} = 0 \qquad (1.27)$$

This function holds for a any given point in the capillary, where c_i and c_i^0 represent the concentration of component i at a given moment in time, and prior

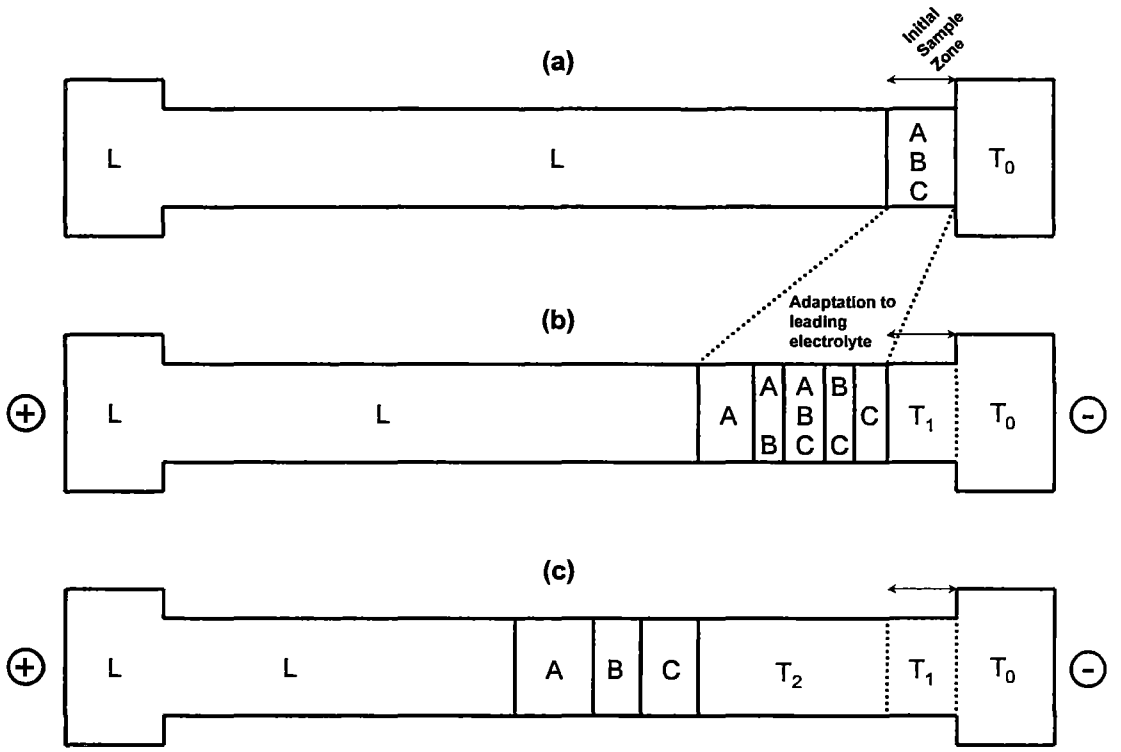

Fig. 1.5 Illustration of an isotachophoretic separation of anions A B C with leading anion L and terminating anion T, and the conditions that $u_L > u_A > u_B > u_C > u_T$. (a) Initial state in the capillary after sample injection. (b) Situation at some time (t_1) after application of driving current. The sample zone has changed to adapt to the leading electrolyte, however the ions present have not completely separated, with mixed zones still present. (c) Complete separation of the three species is achieved at some time ($t_2 > t_1$). Adapted from [213].

to the application of an electric current respectively, and u_i is the electrophoretic mobility of component i. Whilst in general the system is more complex than this, the basic principles are the same.

Descriptively, once a current is applied across the capillary, the ions in the sample start to separate into individual zones in order of decreasing electrophoretic mobility. This is illustrated for an anionic system in Fig. 1.5 with anions A^-, B^-, and C^- leading ion L^- and terminating ion T^-, with the property that $u_L > u_A > u_B > u_C > u_T$. After some time, this process will be complete and there will be three zones with sharp boundaries between the leading and terminating electrolytes, as shown in Fig. 1.5(c). The cations of the system move in the opposite direction. Under constant current conditions (note the difference between this and CE where a constant voltage is usually applied), these bands continue to migrate through the capillary with a constant velocity, hence the name "isotachophoresis". In addition, the zone length of each sample component is proportional to its concentration in solution. This contrasts greatly with chromatographic and CE methods where each analyte appears as a peak, and it is the area or height of this peak which provides the quantitative data. In isotachophoresis, EOF is usually considered an undesirable phenomenon, and is suppressed, for example, through additives to the leading electrolyte.

1.6.5.2 Separation of Sulfur Species by Isotachophoresis

ITP does not enjoy the same popularity as IC and CE, with its use as a distinct analytical technique receding [215], although it currently has a niche as a pre-treatment or pre-concentration tool for other methods [216]. This is reflected in the lower number of references for the determination of sulfur-oxygen species by

this method. Sulfite, sulfate and thiosulfate have been determined in sodium sulfide solutions by ITP [105], using a leading electrolyte of 1:1 water-acetone containing 5 mM hydrochloric acid and 10 mM L-histidine, whilst the terminating electrolyte was 10 mM sodium acetate. Oxidation of sulfide and sulfite in the standards was prevented by using degassed solutions containing 5% glycerine. A further method using 1:1 water-acetone containing 10 mM sodium hydroxide and 0.1% Triton X-100 as the leading electrolyte and 0.01 hexanoic acid as the terminating electrolyte was shown to be suitable for the simultaneous determination of dithionate, tetrathionate and sulfate in addition to other sulfur-oxygen species not considered in this review (peroxodisulfate, $S_2O_8^{2-}$, and disulfate, $S_2O_7^{2-}$) [217]. This method was used in a study of the decomposition of $S_2O_8^{2-}$.

Lucansky *et al.* [218] developed isotachophoretic methodology for the determination of a variety of compounds, including thiosulfate, sulfate and sulfite, in reaction solutions from the preparation of N-morpholino-2-benzothiazolesulphenamide. A variety of leading and terminating electrolyte systems was examined, with the optimal system containing calcium as an additive to separate the chloride and thiosulfate zones. A method also exists for the determination of thiosulfate, sulfate and sulfite in sulfite pulping liquors [219].

ITP has also been used to study oxidation of reduced sulfur compounds by *Thiobacillus ferrooxidans* bacteria [220]. Two methods were required to determine sulfate (first method), thiosulfate and tetrathionate (second method). Both methods used a leading electrolyte containing β-alanine/hydrochloride with

calcium chloride as an additive. The terminating electrolytes were citric acid for the analysis of sulfate and capronic acid for the analysis of thiosulfate. When using the thiosulfate method some unidentified ions were also detected and it was suspected that these were other polythionates present in the sample matrix. Detection limits of 4 and 7 μM were attainable for sulfate and thiosulfate, respectively.

1.6.6 Other Separation Techniques

Various other separation techniques have been used for sulfur speciation, although with the possible exception of ITP, to a much lesser extent than those already discussed. These are discussed briefly below.

1.6.6.1 Planar Chromatographic Techniques

Early research involved the use of paper chromatography and paper ionophoresis to separate sulfur species, particularly the polythionates. These methods have not received significant attention for some years. For further information the reader should consult reviews by Blasius *et al.* [65], Roy and Trudinger [91] or Szekeres [58]. Interestingly, there is one report which describes the use of paper and thin layer chromatography (TLC) [221] to study the gold thiosulfate complex, although the techniques were not used to quantify this ion.

1.6.6.2 Ion-Exclusion Chromatography

Separations using ion-exclusion chromatography (IEC) are few and are mostly concerned with the determination of a single analyte ion, usually sulfite [222-224] or sulfide [225], which are ideally suited to this technique. IEC methods for sulfite have been most commonly applied to foodstuffs and beverages, although the separation of sulfite, sulfide and thiosulfate (in that order) on a mixed

cation/anion exchange resin (Dionex CG5 and CS5 columns in series) using an ion-exclusion eluent [226] has been reported. An iodometric PCR detection method, similar to that already discussed in Section 1.6.3.5, was used [96]. Detection limits were in the range 1.2-6.8 μM.

1.6.6.3 Reversed-Phase-High Performance Liquid Chromatography

The use of reversed-phase HPLC for the separation of ionic sulfur species is uncommon, but sulfite, thiosulfate and sulfide have been determined as their monobromobimane derivatives [189-192]. A peak attributable to polysulfide could also be detected by this method [189], but as with the DTNP derivatisation discussed in Section 3.2.3, this peak could not be quantified.

Reversed-phase HPLC has been used widely for the determination of elemental sulfur precipitate in various aqueous solutions such as seawater [189,192], wastewater [191], solutions of sulfur oxidising bacteria [176,227,228] process waters from a heavy-water plant [229] and sodium thiosulfate injection solutions [230]. Extraction of the sulfur from aqueous solutions with a suitable organic solvent such as methanol [192,227], carbon disulfide [176] or chloroform [189,191,228,229], or cyclohexane [230] is required for the analysis. Henshaw *et al.* [228] examined various parameters for their effect on extraction efficiency, such as agitation time, settling time and the sample matrix. It was observed that extraction of elemental sulfur could be reduced if the sample contained sulfide, as a result of polysulfide formation. This problem was resolved by adding acid to the aqueous solution at the time of extraction to remove the sulfide as H_2S gas. The bio-reactor sample matrix examined was found to cause a negative bias on the results compared to those from elemental sulfur standards. It was hypothesised

that some of the enzymes from the bacteria in the bio-reactor were oxidising a portion of the elemental sulfur, although this was not investigated further. Separation of the various constituent sulfur homocycles (S_x) has also been studied [176]. All these methods used predominantly organic solvent mobile phases to determine elemental sulfur, with the most popular choice being methanol, while UV absorbance was generally used for detection. Detection limits of the methods have ranged between 0.2 μM [230] and 33 μM [191].

1.6.6.4 Gas Chromatography

The use of gas chromatography (GC) for the determination of sulfur anions or elemental sulfur in aqueous solutions has been minimal. The only report using GC involved the determination of elemental and/or polysulfidic sulfur in Kraft pulping liquors [231]. In this method the elemental sulfur was reacted with triphenylphosphine at pH 11.5 and the resulting triphenylphosphine sulfide separated by GC with a flame ionisation detector. Total polysulfide and elemental sulfur was determined in a similar fashion, except that the derivatisation reaction was performed at pH 5.5 where the polysulfide was first converted to elemental sulfur. No detection limit for the method was indicated.

1.6.6.5 Capillary Electrochromatography

Fundamental studies using capillary electrochromatography (CEC) have involved the separation of sulfite, sulfate and thiosulfate [232,233]. Kitagawa *et al.* [232] demonstrated that the elution order for sulfate and sulfite could be reversed by using different applied voltages. The authors performed the separation on a capillary column packed with TSK IC-Anion-SW resin with an eluting electrolyte consisting of 10% methanol and 90% of an aqueous solution containing 5 mM

phthalic acid, 5 mM hexamethylenediamine and 0.15% HEPES (N-2-hydroxyethylpiperazine-N-ethanesulfonic acid).

1.6.7 Analysis of Gold Thiosulfate Leach Solutions

For a significant portion of the literature, the analysis of gold thiosulfate leach solutions has simply involved determining the total leached gold concentration. This is usually found by either atomic absorption spectroscopy (AAS), inductively coupled plasma optical emission spectroscopy (ICP-OES) or indirectly through fire assay. Thiosulfate has been the most common sulfur anion monitored, with determinations reported using titration [39,48,234-236], FIA [44], and IC. Determinations of sulfide (not-detected) [237], sulfite [23,237,238] (not-detected in [237]), sulfate [19,23,56,112,237,238] and polythionates [19,112,237,238] have been performed predominantly using IC methods. Note that the paper by Zou *et al.* [112] did not determine tetrathionate in leach solutions, while Wan [237] did not consider trithionate. At the time of commencement of this project these were the only papers readily available in the literature that considered polythionates in thiosulfate leach liquors.

One problem with some of the existing literature, particularly where IC is used, has been a lack of detail in the experimental methodology making replication of the technique difficult if not impossible. For this reason many of the papers listed in this section are not contained in Tables 1.1 or 1.2. For the papers involving the analysis of polythionates only Zou *et al.* [112] and Molleman and Dreisinger [19] provide any detail at all, and in the latter case a copy of the 1998 Masters thesis referenced in this work would be required for the complete methodology used.

However, more detail of what is presumed to be the same method was given in another recent paper from the same research group [239].

To date, no detailed method has been reported that can simultaneously determine sulfite sulfate, thiosulfate and the polythionates in the leach.

1.7 Aims of Project.

This review has shown that there is much that can be done to improve the existing methodology for analysis of gold thiosulfate leach liquors in order to assist in the provision of essential information to better understand and develop the thiosulfate leaching process for gold ores. It would appear that significant dilution of samples is required for many of the techniques used for analysis of the sulfur-oxygen anions which may to some extent compromise the accuracy of the results. There is no reported methodology that can simultaneously determine all the sulfur-oxygen anions of interest in leach solutions while a capability to perform faster analyses would also be advantageous. No evidence exists of investigations into the utility of CE or ITP for gold thiosulfate leach solutions and it would appear that the analysis of metal thiosulfate complexes by any separation technique has largely been ignored altogether.

Therefore the general aim of this work was to develop chromatographic and electromigrative methods for the separation of sulfur anions and complexes pertinent to gold thiosulfate leach solutions. Specific aims of the project were to:

- Investigate the ion-chromatographic and electrophoretic behaviour of the gold thiosulfate complex.

- Develop improved ion-chromatographic methodology for the determination of sulfur-oxygen species in leach solutions.
- Investigate the utility of electromigrative methods for the gold thiosulfate and sulfur-oxygen anions.

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Chapter 2

General Experimental

This section describes the chemicals and procedures that were used throughout this work. Because the project involved three distinct analytical techniques, the instrumental and other details pertaining to each of these methodologies are described in the relevant chapters.

2.1 Reagents

2.1.1 Commercially Available Compounds

The chemicals used are listed in Table 2.1 and were of analytical reagent grade unless otherwise specified.

2.1.2 Polythionate Synthesis and Purification

Potassium trithionate ($K_2S_3O_6$) and potassium pentathionate sesquihydrate ($K_2S_5O_6.1.5H_2O$) were not available commercially. Quantities of these salts were generously provided by Professor Yasuyuki Miura of Tokai University, Japan. Postassium trithionate was prepared according to the methods of Stamm *et al.* [1] and recrystallised after arrival in Tasmania from water initially at 35°C, via cooling in an ice-bath. The resulting crystals were filtered off and washed with acetone. Potassium pentathionate ($K_2S_5O_6.1.5H_2O$) was prepared according to the method of Goehring and Feldmann [2], and was recrystallised twice from 2 M hydrochloric acid initially at 60°C.

The commercial sodium tetrathionate ($Na_2S_4O_6.2H_2O$, 98%, Aldrich) required further purification to remove insoluble elemental sulfur. This was achieved

Table 2.1 Chemicals utilised in this project.

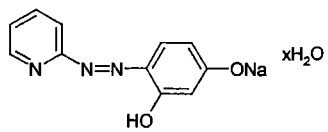
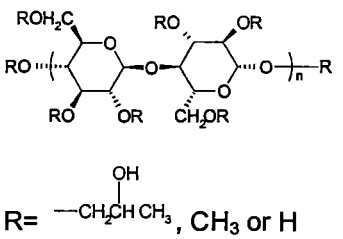
Compound	Formula	Supplier
Acetylene	$HC \equiv CH$	BOC Gases, Chatswood, NSW, Australia.
2,2-bis(hydroxymethyl)-2,2',2''-nitrilotriethanol	$(HOCH_2CH_2)_2NC(CH_2OH)_3$	Aldrich Chemicals, Milwaukee, WI, USA.
4-(2-pyridylazo)resorcinol monosodium salt hydrate		Aldrich
Acetone	CH_3COCH_3	Chem-Supply, Gillman, SA, Australia.
Acetonitrile (HPLC Grade)	CH_3CN	BDH Chemicals, Kilsyth, Vic., Australia.
Ammonia (28% w/w)	NH_3	APS Chemicals, Auburn, NSW, Australia.
Ammonium sulfate	$(NH_4)_2SO_4$	BDH Chemicals
Ammonium thiosulfate	$(NH_4)_2S_2O_3$	Reidel-de-Haen, Seelze, Germany.
Copper sulfate pentathydrate	$CuSO_4.5H_2O$	BDH Chemicals
Ethanol	CH_3CH_2OH	BDH Chemicals
Formic acid	HCOOH	Prolabo, Paris, France.
Glacial acetic acid	CH_3COOH	BDH Chemicals
Gold (99.99%)	Au	The Perth Mint, WA, Australia.
Hydrochloric acid (36% w/w)	HCl	BDH Chemicals
Hydroxypropylmethylcellulose Average M_n *ca.* 12,000. 21 wt. % methoxy, 5 wt.% propylene oxide.	 R= , CH_3 or H	Aldrich
Methanol (HPLC Grade)	CH_3OH	BDH Chemicals
Nitric acid (69% w/w)	HNO_3	BDH Chemicals
Nitrogen	N_2	BOC Gases

Table 2.1 (Cont.)

Compound	Formula	Supplier
Phosphoric Acid (88% w/w)	H_3PO_4	BDH Chemicals
Potassium dihydrogen phosphate	KH_2PO_4	BDH Chemicals
Potassium sulfate	K_2SO_4	BDH Chemicals
Sodium acetate	$NaOOCCH_3$	APS Chemicals
Sodium carbonate	Na_2CO_3	BDH Chemicals
Sodium chloride	NaCl	May and Baker, West Footscray, Vic., Australia.
Sodium formate	NaOOCH	APS Chemicals
Sodium gold thiosulfate dihydrate	$Na_3Au(S_2O_3)_2.2H_2O$	Alfa Aesar, Ward Hill, MA, USA.
Sodium hydroxide	NaOH	APS Chemicals
Sodium Iodide	NaI	Aldrich
Sodium perchlorate	$NaClO_4$	Aldrich
Sodium sulfate	Na_2SO_4	Prolabo
Sodium thiocyanate	NaSCN	Aldrich
Sodium thiosulfate pentahydrate	$Na_2S_2O_3.5H_2O$	BDH Chemicals
Sulfuric acid (98% w/w)	H_2SO_4	APS Chemicals
Tetrabutylammonium chloride hydrate	$[CH_3(CH_2)_3]_4NCl.xH_2O$	Aldrich
Tetrabutylammonium hydroxide (40% w/w solution)	$[CH_3(CH_2)_3]_4NOH$	Aldrich
Waters PIC-A low UV Reagent (Tetrabutylammonium hydrogen sulfate in water-methanol mixture)	$[CH_3(CH_2)_3]_4NHSO_4$	Waters

by dissolving a portion of the salt in a minimal amount of water, filtering the solution (0.45 μm, Gelman Scientific, Lane Cove, NSW, Australia, and then re-precipitating the salt through the addition of ethanol.

All polythionates used were dried at room temperature (if required) and thereafter stored below -5°C.

2.1.3 Sodium Gold Thiosulfate Dihydrate

Some of the work described in Chapter 3, which was conducted prior to the acquisition of a commercial standard, used sodium gold thiosulfate prepared in-house. Three methods were attempted [3-5], for the synthesis of this compound, with the tetrachloroauric acid precursor also being prepared according to literature methods [6]. Out of these techniques the best purity obtained was through methodology based on that of Tavernier and de Meyer [4] from which a crop of crystals was obtained and analysed to be ~89% pure based on gold content by ICP-OES. The main impurity was determined to be sodium thiosulfate. The compound was stored below 4°C.

2.1.4 Gold Ore Samples

The sulfidic (approximate gold concentration of 50 ppm) and oxide (approximate gold concentration of 220 ppm) ore/concentrates used in this project were supplied by Osleach Pty. Ltd. (Currumbin, Qld., Australia).

2.2 Procedures

2.2.1 General Eluent, Electrolyte and Standard Preparation Procedures

All sample solutions, eluents and electrolytes were prepared in water purified using a Millipore Milli-Q (Bedford, MA, USA) purification system. All IC eluents and bulk electrolyte solutions for the CE replenishment system were filtered through a nylon 0.45 μm filter (Alltech Associates Pty. Ltd., Baulkham Hills, NSW, Australia), prior to use. All other CE electrolytes were filtered through a 0.45 μm syringe filter (Gelman Scientific, Lane Cove, NSW, Australia).

2.2.2 Leaching Experiments

Leaching of gold bearing ores was conducted in a 1000 mL, 3-neck, flat-bottomed flask. A sample (100 g) of the ore under investigation was slurried in water and added to the flask, followed by 6.24 g of copper sulfate and 69 mL of concentrated aqueous ammonia. The solution was made to a volume of ~470 mL with distilled water, heated to 50±3°C and mechanically agitated with an overhead stirrer at ~140 rev/min (for test of IC method) or ~120 rev/min (for test of CE method). The stirring arm used was glass with Teflon paddles. A condenser was fitted to the flask to minimise evaporation. When the solution reached the required leach temperature, 37.05 g of ammonium thiosulfate was added with the aid of distilled water to give a final volume of 500 mL. The time at which the thiosulfate was added to the leach was denoted zero time.

For sampling, the condenser was removed and approximately 6 mL (IC method) or 3 mL (CE method) samples were removed from the leach solution with stirring

still in progress. The solid present in the sample was removed by filtration through a 0.45 μm nylon syringe filter, and the samples analysed immediately.

2.2.3 Calculations

For IC, retention data are often reported as the retention factor (k'), which for a solute is defined as,

$$k' = \frac{t_R - t_0}{t_0} \qquad (2.1)$$

where t_R is the retention time of the solute, and t_0 is the time taken for an unretained solute to pass through the same system to the detector.

For CE, the effective mobility (μ_{eff}) for a given solute was calculated according to Eqn 2.2,

$$\mu_{eff} = \frac{L_T L_D}{V t_M} \qquad (2.2)$$

where L_T is the length of the capillary in metres, L_D the length the capillary to the detector in metres, V is the applied voltage in volts, and t_M is the migration time of the solute in seconds.

2.3 References

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Chapter 3

Fundamental Behaviour of the Gold Thiosulfate Complex in an Ion-Chromatographic System

3.1 Introduction

Knowledge of the concentration of gold in solution during and after a leach is of critical importance in the assessment and monitoring of any hydrometallurgical process for extraction of this metal. As noted in Chapter 1, for a significant portion of the literature on the thiosulfate process the only leach parameter determined was the gold concentration in solution or percentage gold extracted. The techniques used for this determination, namely, AAS, ICP-OES and fire assay, do not allow identification of the gold species present in solution, nor the concentrations of the other critical species in the leach, such as thiosulfate, the polythionates and sulfate. The effectiveness of chromatographic methods to quantify the gold present in these solutions has not previously been examined.

As also noted in the literature review, the predominant if not only, gold species in the leach solutions is thought to be the bis-thiosulfate complex ($Au(S_2O_3)_2^{3-}$). The lack of previous information on the behaviour of this ion in chromatographic systems and the above-mentioned importance of gold monitoring to the leach process made a fundamental chromatographic study of this species an important part of the project. Ion-interaction chromatography was chosen as the focus for this work because of its previous use for the determination of gold and other metal cyanide species in gold cyanide leach solutions [1-4]. Additionally, the technique is the method of choice for determination of the polythionate ions, which as

previously noted will also require quantification in leach liquors. The use of the same technique for the gold complex was therefore desirable as it provides the most likely means of allowing simultaneous analysis. The choice of the main column (Dionex NS1) and eluent system (acetonitrile-water/tetrabuytlammonium hydroxide (TBAOH)/Na_2CO_3) was also made on the basis that this system has been used widely for the determination of polythionate ions.

This chapter outlines the results of this fundamental study into the chromatographic behaviour of the gold thiosulfate complex.

3.2 Experimental

3.2.1 Chromatographic Instrumentation

The ion-chromatograph used in this investigation was a Dionex DX-500 (Sunnyvale, CA, USA) system consisting of a GP50 gradient pump, AS50 autosampler with thermal compartment, CD20 conductivity detector, AD20 ultra-violet/visible (UV/VIS) absorbance detector and/or a Waters (Milford, MA, USA) 486 UV detector, the latter connected to the data system via a Dionex UI20 universal interface. A pump flow rate of 1.0 mL/min, column oven temperature of 35°C and a 100 µL injection loop were used unless otherwise specified. For UV detection a wavelength of 215 nm was used, whilst conductivity detection was performed with suppression provided by a Dionex ASRS-Ultra operated in the chemical suppression mode. The regenerant (usually 5 mM sulfuric acid) was delivered by a Waters 510 high performance liquid chromatography (HPLC) pump at a flow rate of 4.0 mL/min, again unless otherwise specified. All chromatographic data were collected using Dionex PeakNet software version 5.1.

For the anion-exchange work (Section 3.3.1.1), a Dionex EG40 eluent generator module with a potassium hydroxide EluGen cartridge was fitted to the instrument to generate the hydroxide based eluents required.

For photodiode array (PDA) detection of the gold thiosulfate complex (Section 3.3.1.1), a Waters Alliance 2690 HPLC instrument was used, fitted with a Waters 996 PDA detector. The chromatograms obtained were scanned between 200-600 nm at 1.2 nm intervals, with the data collected using Waters Millennium software (version 3.05.01).

The research using a matrix elimination pre-column was facilitated by the use of two Valco ChemInert 6-port, 2-position switching valves with electronic actuators (Valco Instrument Co. Inc., Houston, TX, USA). Programming actuation of each valve from the PeakNet software was achieved with two relay switches on either the CD20 or GP50 instrument modules. The configuration of the valves was based on a system previously described by Haddad and Rochester [5], with the main modification to include the autosampler, which removed the need for the sample to pass through the chromatographic pump. The modified system is illustrated graphically in Fig. 3.1, and the program required to execute the matrix-elimination procedure is shown in Table 3.1.

3.2.2 Columns and Eluents

Several different columns were used through the course of this investigation. The majority of the experiments were carried out on a Dionex NG1 (4 x 50 mm) and

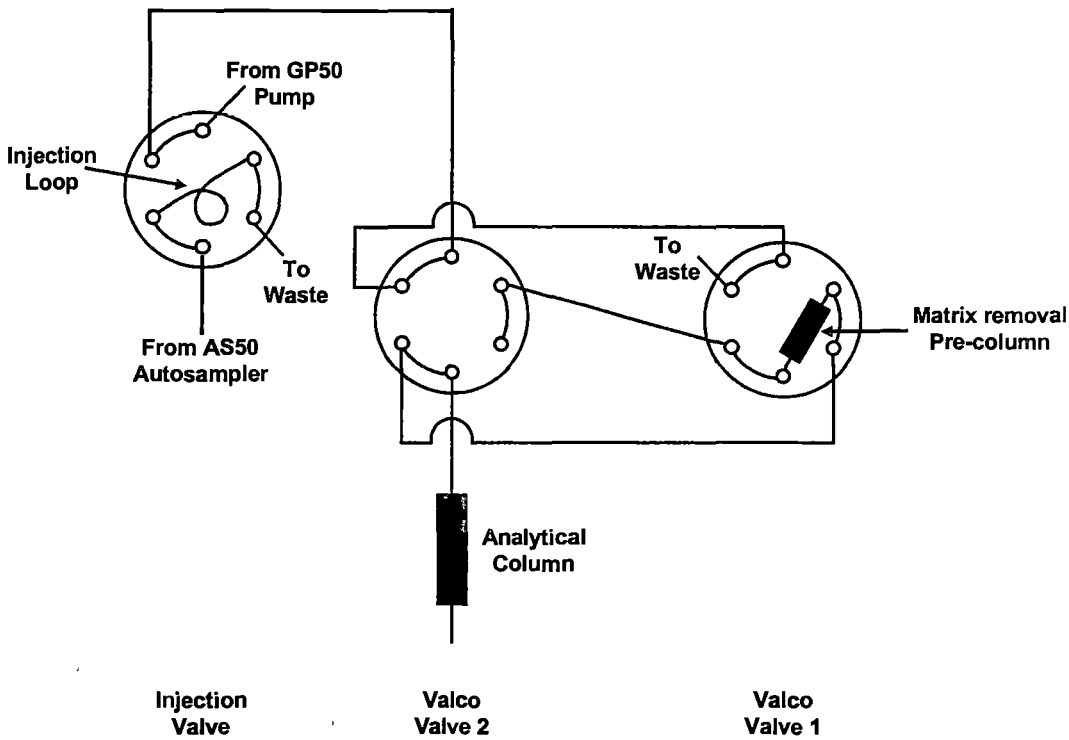

Fig. 3.1 Diagram showing switching valve configuration and associated tubing, for the matrix-removal pre-column procedure. All valves shown in position "A".

Table 3.1 Switching valve program for matrix-elimination column procedure. Eluent A = eluent for matrix elimination, Eluent B = eluent for backflush and analysis.

Time (minutes)			Initial	0 00	0 01	0 04	0 05	0 10	0 85	0 90	0 95	1 00	1 20	1.25	5 20	8 19	8 20	8.25	8 30	8 35	9 20	9.25	9 30	9.35	9 60	9.65
Module	AS50			LOAD											INJECT												
	GP50	Eluent	B	B	A											A	B										
		Flow Rate (mL/min)		1		1	3	5	4	3	2	1				1			3	5	4	3	2	1			
		Relay State	Relay 1 ON	Relay 1 OFF									Relay 2 ON	Relay 2 OFF											Relay 1 ON	Relay 1 OFF
	CD20	Relay State	Relay 2 ON	Relay 2 OFF	Relay 1 ON		Relay 1 OFF								Relay 2 OFF	Relay 2 ON		Relay 2 OFF								
		Other													Offset Begin Data Acquisition											
	UI20														Begin Data Acquisition											
	Switching Valve 1 Position		B										A												B	
	Switching Valve 2 Position		A		B											A										

NS1 (4 x 250 mm) in series, although in some cases a NS1-5 μ (4x 150 mm) column was employed in place of the NS1. Other columns examined were the Dionex AG16 guard (4 x 50 mm), Waters NovaPak C_{18} (3.9 x 150 mm) and the Zirchrom DiamondBond C_{18} (4.6 x 100 mm, Zirchrom Separations Inc., Anoka, MN, USA).

For the majority of experiments the ion-interaction eluents were prepared manually, without on-line mixing. Mixing stock solutions on-line to generate the eluents was simpler, but the disadvantage of this was a significantly higher baseline noise. Solvent degassing during mixing and/or noise from the gradient pump was the suspected cause of this problem. Off-line mixed eluents gave lower noise, but there was sometimes significant variation in retention times between batches of eluent, suspected to occur through irreproducible loss of acetonitrile during vacuum filtering.

Three main column/eluent configurations were used in this work and in this chapter they will be abbreviated I, II or III as follows:

I Dionex NG1 + NS1 in series with eluent containing 28% *v/v* acetonitrile, 3 mM TBAOH and 2 mM Na_2CO_3.

II As above, except with 40 μM thiosulfate added to the eluent.

III Dionex NG1 + NS1-5μ in series with eluent containing 28% *v/v* acetonitrile, 3 mM TBAOH and 2 mM Na_2CO_3.

The eluent program used for the anion-exchange work had an initial concentration of 5 mM KOH stepping to 90 mM KOH at 4.0 min and returning to 5 mM KOH

at 9 min. Seven minutes were allowed for re-equilibration prior to injection of the next sample.

3.2.3 Spectroscopic Instrumentation

The AAS used for all fraction collection studies was a Varian SpectrAA-800 (Varian, Mulgrave, Vic., Australia), equipped with a GTA-100 graphite furnace accessory. A variety of conditions was used for the studies employing the graphite furnace instrument, all based on the default program for gold [6]. Most modifications involved slower sample addition, a lower initial furnace temperature, and/or a significantly slower drying stage. These attempted to prevent sample losses from occurring as a result of the high sample acetonitrile content. Gold absorbance was measured at 242.8 or 267.6 nm using a Photron (Photron, Narre Warren, Vic., Australia) gold hollow cathode lamp.

Experiments using the flame AAS mode were conducted using an air (13.68 L/min)-acetylene (1.93 L/min, BOC Gases, Chatswood, NSW, Australia) flame. The gold signal was measured at 242.8 nm, with the implied concentrations calculated using standards (2-30 μM) prepared in the chromatographic eluent. The column fractions taken in these experiment were 0-4, 4-8, 8-12 and 12-16 mins.

3.2.4 Column Digest Procedure (Adapted from [7])

The column digest (Section 3.3.1.4) was performed by first removing the packing from the column and drying at 100°C for 50 min. Approximately 12 mL of concentrated (98%) H_2SO_4 was added to the resin and charred by boiling the solution (~200°C). After this the temperature was reduced to ~150°C, 17 mL of concentrated (70%) HNO_3 was added dropwise and then the solution boiled again,

until clear. After cooling to ~ 50°C 10 mL of concentrated (32%) HCl was added dropwise to the digest. After cooling, the solution was diluted to a final volume of 50.00 mL with milli-Q water and analysed for gold by AAS.

3.3 Results and Discussion

3.3.1 Investigation into the Ion-Chromatographic Behaviour of the Gold Thiosulfate Complex in the Absence of Other Matrix Ions

3.3.1.1 Preliminary Investigations

The behaviour of the gold thiosulfate complex was first investigated without the presence of other matrix ions, using an ion-interaction system consisting of Dionex NG1 and NS1 columns in series, and eluents comprising acetonitrile-water mixtures containing TBAOH and Na_2CO_3. The standards used were prepared simply by dissolving a portion of sodium gold thiosulfate dihydrate ($Na_3Au(S_2O_3)_2.2H_2O$) in milli-Q water. A typical chromatogram for such a standard is shown in Fig. 3.2(a). It can clearly be observed that there is a thiosulfate peak and a raised baseline joining it to a second much more strongly retained peak. A similar chromatogram was observed regardless of whether conductivity or UV detection was used. An anion-exchange system was also found to demonstrate the same behaviour (Fig. 3.2(b)), although UV detection was not investigated in this case. Column fractions from injections of the gold complex were analysed using graphite furnace atomic absorption spectroscopy (GF-AAS) and this confirmed qualitatively (Fig. 3.2(a)) that the main plug of gold eluted in the zone corresponding to the second peak, which was therefore attributed to the gold thiosulfate complex. Results also suggested that there was a small amount of gold in the latter half of the raised baseline region, and also after

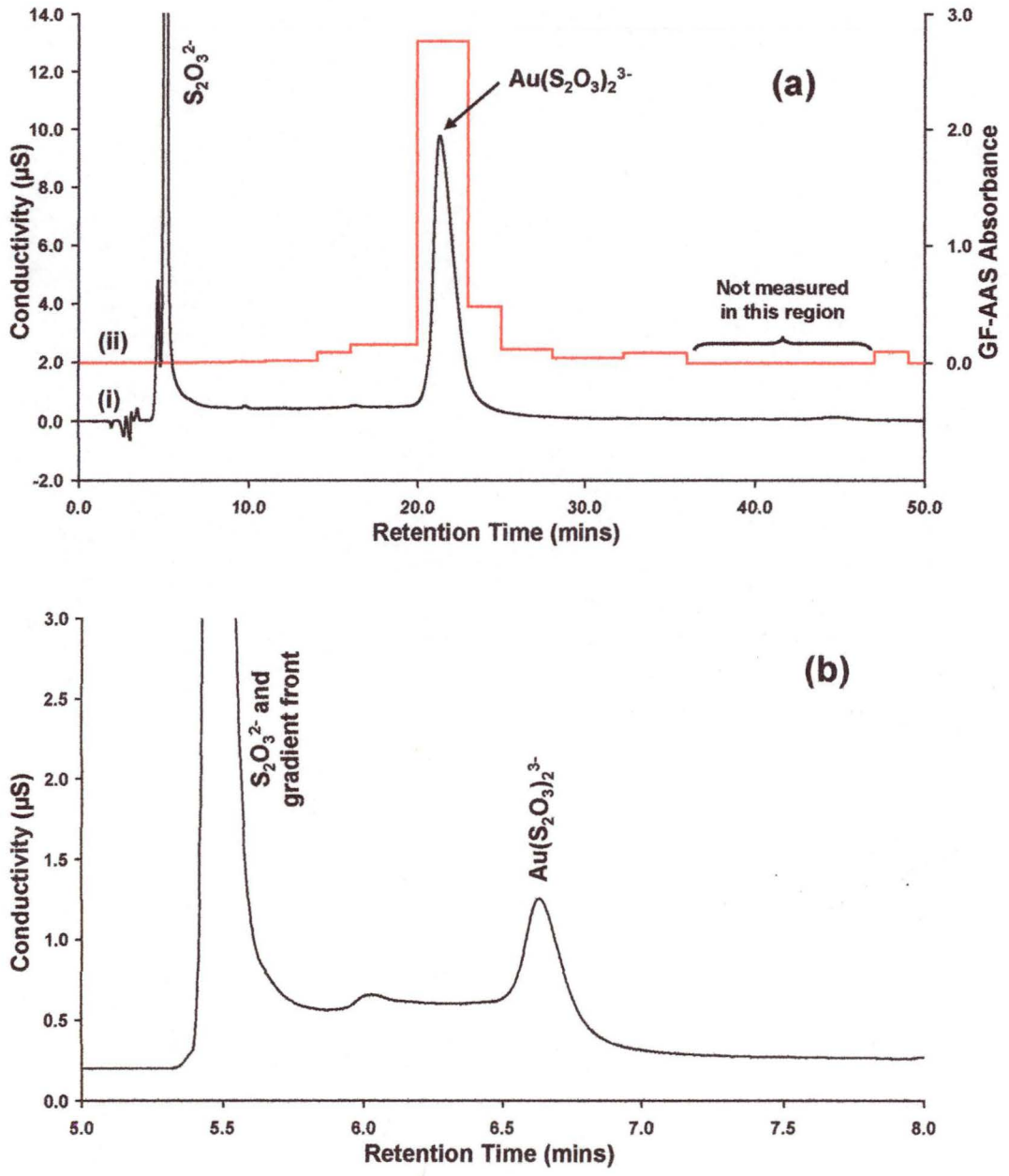

Fig. 3.2 (a) (i) Injection of gold thiosulfate solution containing 0.914 mM (180 mg/L) Au(I), prepared from ~89% pure sodium gold thiosulfate dihydrate prepared in house. Conditions: (I), with suppressed conductivity detection, and 25 µL injection volume. **(ii)** Results of column fraction analysis of this injection for gold at 242.8 nm by GF-AAS **(b)**, Gold solution prepared from the same standard containing 0.094 mM (18.5 mg/L) Au(I). Conditions: 2 x Dionex AG16 guard columns, with hydroxide eluent program as described in Section 3.2.2, suppressed conductivity detection (external water mode) with current of 300 mA, regenerant flow rate of ~2 mL/min, provided by headpressure and a 10 µL injection volume.

the gold peak, as is also evident from Fig. 3.2 (a). Note that the impure gold standard used for this preliminary work would have contained a small amount of thiosulfate impurity. However, as will be described later in the chapter this affected the gold peak area, but not the observed shape of the chromatogram. Quantification was not possible since recoveries were extremely high, for reasons that could not be determined. With the location of the main gold peak verified its spectrum was obtained between 200 and 600 nm to determine the optimum wavelength of detection, with the result given in Fig. 3.3. No spectrum for the complex could be found in the literature. Whilst detection of the complex seems more sensitive at wavelengths around 200 nm, 215 nm continued to be used as a compromise between maximising the sensitivity of the gold thiosulfate chromophore and minimising the background noise of the eluent.

The appearance of the raised baseline suggested that there was some form of partial dissociation or decomposition of the complex on the column. This immediately raised questions about the cause(s) of this effect and its influence on quantification of the gold complex by this technique. The detection limit and linearity of the gold peak were therefore investigated to assess the effect on quantification. The detection limit of the gold thiosulfate complex appeared not to be a function of the detection sensitivity. Instead, a critical concentration of the complex had to be injected before a portion would traverse the entire column in its original form and this determined the lowest detectable concentration. This effect is demonstrated in Fig. 3.4, showing an overlay of a series of progressively

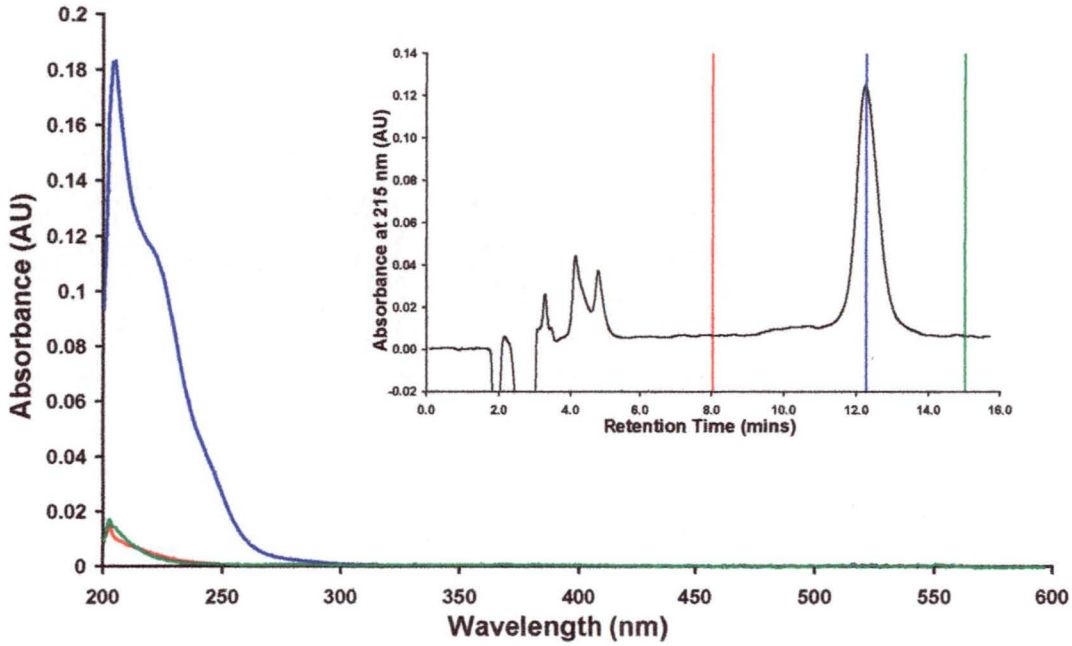

Fig. 3.3 UV-visible spectra of the gold thiosulfate complex (blue line) obtained from an injection of a 0.196 mM (38.6 mg/L) solution (as gold), with a spectra of the raised baseline region (red line) and after the gold peak (green line) shown for comparison. Inset shows chromatogram (215 nm) indicating where the spectra were extracted. Conditions (I), no eluent suppression was used.

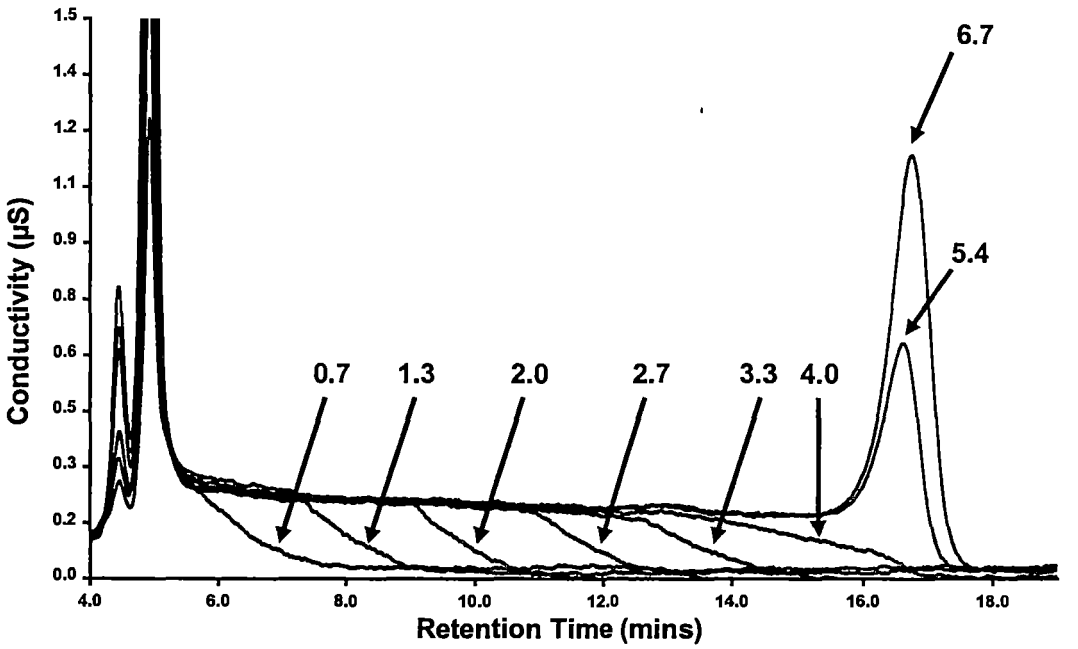

Fig. 3.4 Conductivity chromatograms from injection of a series of gold thiosulfate solutions prepared from ~89% pure sodium gold thiosulfate dihydrate, containing the indicated concentrations of gold (mg/L). Conditions: (I). UV results at 215 nm were similar.

increasing concentration gold standards. The length of the raised baseline increased with increasing gold concentration, until finally enough was injected for the gold peak retention time to be reached. The injection of gold thiosulfate at concentrations between 0.046 and 0.228 mM (9 and 45 mg/L) as Au(I) showed non-linear behaviour, with a quadratic curve more accurately describing the shape of the graph.

3.3.1.2 Addition of Thiosulfate to the Eluent

The first hypothesis proposed to explain the cause of the thiosulfate peak and raised baseline was dissociation of the gold thiosulfate complex in solution and during the transition of the complex through the column, for example:

$$Au(S_2O_3)_2^{3-} \rightleftharpoons S_2O_3^{2-} + Au(S_2O_3)^- \qquad (3.1)$$

The raised baseline started immediately after the elution of the thiosulfate peak, suggesting that thiosulfate contributed to this effect, which was consistent with this hypothesis. If this was the cause, the rate at which this occurred must be relatively slow compared to the speed of separation, as fast kinetics would result in a single peak representing the average form of the associated and dissociated complexes. Also, the addition of a small amount of thiosulfate to the eluent should hinder dissociation and therefore prevent the formation of the raised baseline. A similar approach has been successfully employed for copper(I) cyanide complexes, in which cyanide was added to the eluent to reduce dissociation and improve the peak shape [2,4].

Accordingly, the behaviour of the gold complex was examined in a series of eluents of the same composition, apart from changes in the thiosulfate

concentration present. An overlay of the resultant chromatograms is provided in Fig. 3.5, demonstrating that the addition reduced but did not completely resolve the raised baseline problem. It should be noted that the presence of thiosulfate in the eluent increased the baseline noise for both conductivity and UV detection, as the species cannot be suppressed in this system and absorbs at the wavelength used for UV detection. The detection limit experiment previously shown in Fig. 3.4 was repeated, but in this instance the eluent contained 40 μM thiosulfate, and showed similar behaviour to that observed without the thiosulfate addition. However, it was not possible to determine whether the free thiosulfate peak observed previously in gold thiosulfate samples had disappeared. The addition of thiosulfate to the eluent caused a system peak at the retention time of thiosulfate that prevented such an assessment.

It was also apparent that adding thiosulfate to the eluent markedly increased the gold thiosulfate peak area, induced linear gold calibration curves (Fig. 3.6(a)) and improved the peak area reproducibility (Fig. 3.6(b)). Fig. 3.6(a) also demonstrates that there appeared to be an optimum concentration of thiosulfate with the addition of 100 μM giving slightly lower peak areas at higher gold concentrations than the 40 μM eluent. From Fig. 3.6(b) it is clear that even the presence of only 10 μM thiosulfate in the eluent significantly improved the %RSD values for the gold peak area.

Finally, linearity was tested over a greater range corresponding to an Au(I) concentration of 0.0508-0.508 mM (10 to 100 mg/L) using IC conditions (III).

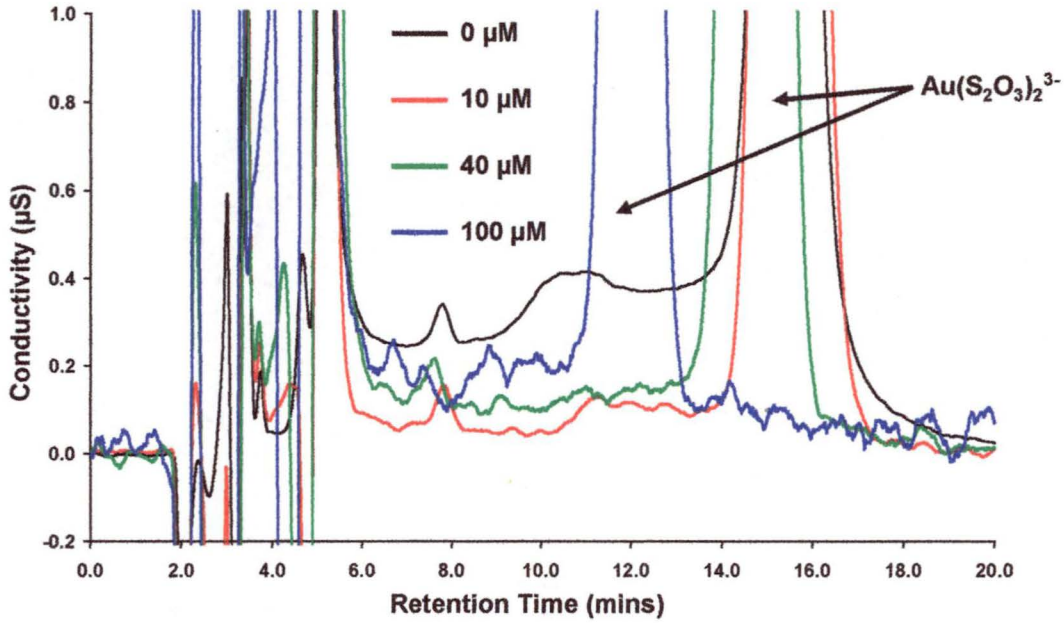

Fig. 3.5 Effect of the eluent thiosulfate concentration on the raised baseline from injections of matrix free gold thiosulfate solutions containing 0.139 mM (27.4 mg/L) Au(I). Conditions: (I), except for thiosulfate content of eluent.

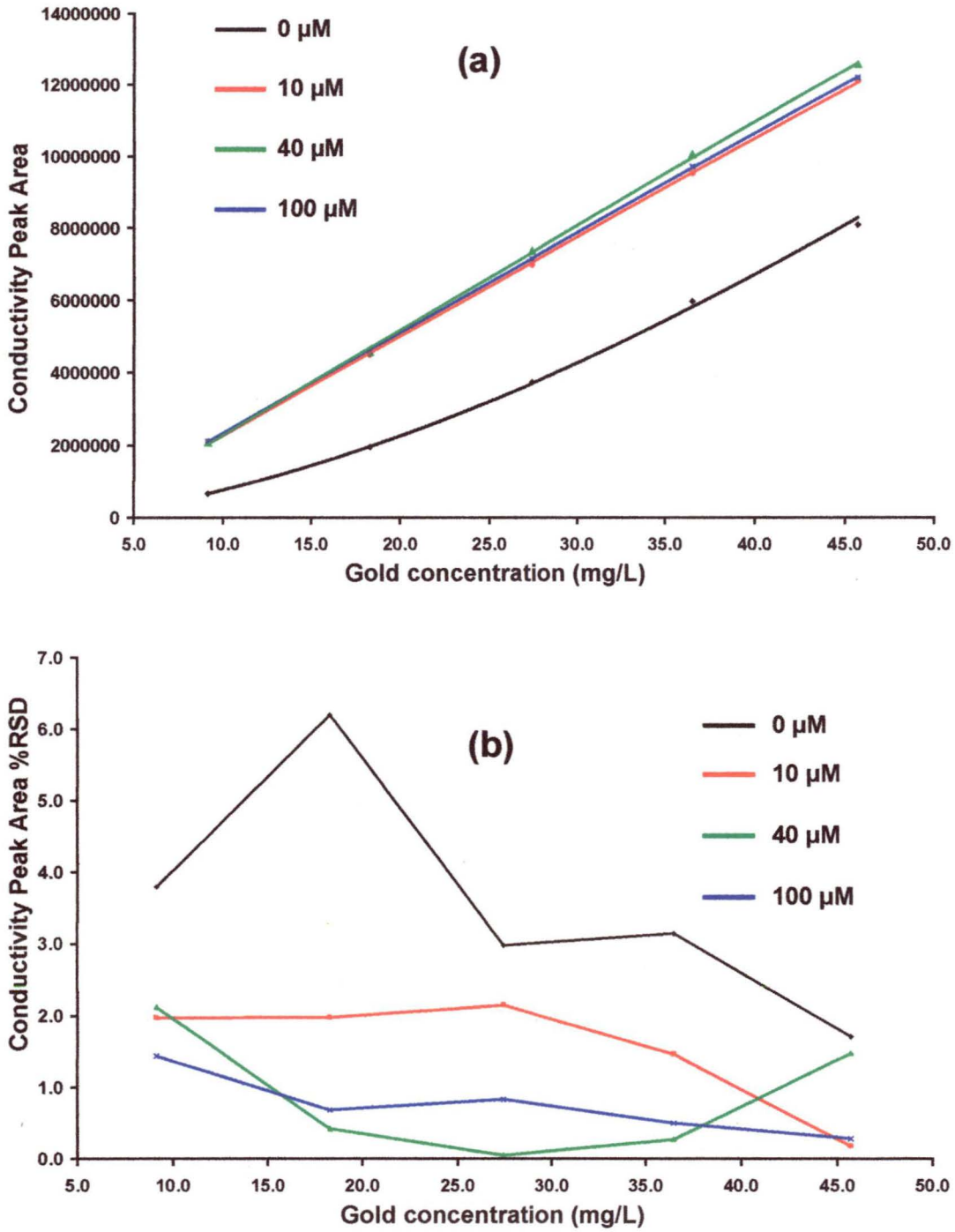

Fig. 3.6 Effect of adding thiosulfate to the eluent on **(a)** linearity and **(b)** peak area %RSD values for matrix free standards of gold thiosulfate. Conditions: (I), except for thiosulfate concentration of eluent.

Linear calibration was observed (R^2 >0.9995) for both conductivity and UV detection over this range.

Investigations into the use of thiosulfate-containing eluents suggested that whilst complex dissociation may be significant on the column and be reduced by the addition of thiosulfate to the eluent, this was not the only mechanism at work, as shown by the continued observation of a raised baseline. Further investigation was therefore warranted.

3.3.1.3 Use of a Silica C_{18} Column

Another hypothesis considered was that the stationary phase, in this instance the polymer based backbone of the Dionex NS-1 column, may have catalysed the decomposition of the gold complex in some manner. To investigate this it was decided to try a Waters NovaPak C_{18} column and a 25% *v/v* acetonitrile-water mixture containing 5mM Waters low-UV PIC-A ($TBAHSO_4$), as eluent. This method has previously been used for determination of the gold cyanide complex ($Au(CN)_2^-$) in cyanide leach solutions [8]. $TBAOH/Na_2CO_3$ based eluents, described in the preceding sections, were not used in this study because of the instability of silica-based columns in alkaline solutions. Results for this column, obtained without thiosulfate in the eluent, are illustrated in Fig. 3.7. Retention was lower in this system, however the same problems were evident. In contrast to the polymer column, the raised baseline continued past the gold peak. Trithionate and tetrathionate could not be responsible for forming this raised zone, since trithionate was eluted between thiosulfate and the gold complex, whilst tetrathionate co-eluted with the gold. Sulfate and sulfite should show lower retention than thiosulfate, whilst the formation of higher polythionates was

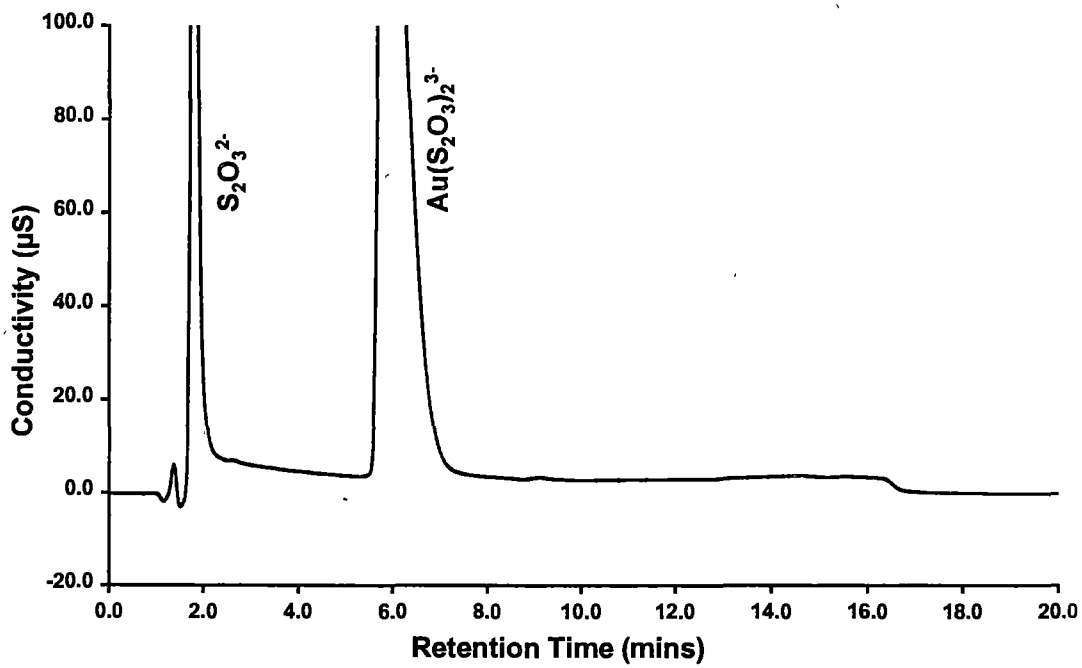

Fig. 3.7 Effect of using a silica based C_{18} column and corresponding eluent, on the chromatography of the gold thiosulfate complex, shown here for a solution containing 0.707 mM (139.3 mg/L) gold, prepared from ~89% pure sodium gold thiosulfate dihydrate. Conditions: Waters NovaPak C_{18} column with corresponding guard inserted in a Waters Guard-PAK module, eluent consisting of 25% *v/v* acetonitrile containing 5 mM Waters low-UV PIC-A reagent (5 mM $TBAHSO_4$), 25 µL injection volume and UV detection at 215 nm.

unlikely. One hypothesis that may explain the result was that the raised baseline following the main gold peak was caused by the gold monothiosulfate complex, although spectroscopic studies were not conducted to determine where the gold was eluted. Also, the lack of information on this species in the literature, other than that it exists [9], makes it difficult to assess whether the complex would be formed or would survive long enough, to be observed in the chromatogram.

Using the same eluent on the Dionex NS-1 column produced similar results to those observed with the TBAOH/Na_2CO_3 eluent.

3.3.1.4 The Possibility of Gold Precipitation on the Column

The above investigation provided no satisfactory explanation of why the raised baseline continued to be present even after the addition of thiosulfate to the eluent. Another possible mechanism would be that a portion of the gold actually precipitated on-column and the residual raised baseline was due to the soluble component of the complex remaining after this had occurred.

To test this hypothesis, an old guard column that had been used extensively in the work for this chapter was digested in acid and the resulting solution analysed by AAS. The results were negative, but this in itself did not eliminate the theory from further consideration since it was possible that the gold was remobilised by other solutions, such as thiosulfate leachates, which had passed through the column.

During experiments examining the gold content of column fractions by flame AAS, the primary results of which will be discussed in greater detail later in the thesis, evidence of on-column gold precipitation was observed. In column

fractions resulting from the injection of a synthetic leach sample containing, 0.5 M $(NH_4)_2S_2O_3$, 2 M NH_3, 0.05 M $CuSO_4$ and 0.508 mM (100 mg/L Au(I)) added as the thiosulfate complex, the gold recovery was 235% (IC conditions (III) were used in this study). Because of the inaccuracies inherent in the analytical method used, recoveries of between 110-120% were routinely observed for injections of gold standards. Even taking this into consideration the observed recovery value was nearly twice that of any other sample investigated. An examination of the column history indicated that prior to this sample, a large number of injections of gold thiosulfate standards containing either no or only low concentrations of other matrix ions had occurred. Further leach solution injections made two days later gave gold recoveries much closer (118-126%) to those obtained for the gold standard alone (111-120%). The only difference in this second set of injections was that a much lower mass of gold in standards containing no or low concentrations of matrix ions had passed through the IC system prior to the leach sample. These results therefore supported the theory that there was a significant amount of gold already on the column in the first experiment and this had been mobilised by the injection of a leach solution.

3.3.1.5 Effect of Ion-Interaction Eluent Acetonitrile Purity on Gold Thiosulfate Chromatography

During one experiment, the brand of acetonitrile used was changed from BDH Chemicals HighPerSolv far UV-grade, purity 99.9% (Product No. 15251) to APS Chemicals 210 nm Grade, Unichrom, purity 99.7% (Product No. 2316). This change was also found to have a major impact on the chromatography, with retention time of the gold thiosulfate complex decreasing and the raised baseline between the thiosulfate and gold thiosulfate increasing. Switching back to the

BDH acetonitrile resolved the problem, indicating that some interaction between the gold and an impurity in the APS acetonitrile had occurred. However, the identity of this compound was not established. Nitriles, such as malononitrile, have been investigated as alternative lixiviants for gold [10] so it should not be surprising that impurities in acetonitrile could form an alternative complex with the gold present.

3.3.1.6 Conclusions from the Investigation of Gold Thiosulfate Solutions Not Containing Matrix Ions.

The analysis of gold thiosulfate solutions in the absence of other matrix ions showed the presence of a raised baseline of unknown composition, although thiosulfate was suspected to be one of the components. This behaviour was at least in part attributable to dissociation of the gold thiosulfate complex on column, and could be minimised by the use of thiosulfate in the eluent. However, this addition did not completely remove the raised baseline. This led to the consideration that some of the gold precipitated on the column, a hypothesis that was supported by the observation that injection of a synthetic thiosulfate leach solution after a large number of gold thiosulfate standards gave over a 200% gold recovery in column fraction analysis by AAS. The use of a silica based C_{18} column did not offer any improvement over the polymer material used for the majority of this work.

Regardless of the mechanism(s) at work, when thiosulfate was present in the eluent the processes involved were quite reproducible and the detection of the gold thiosulfate complex gave linear calibrations at least between 0.0508-0.508 mM (10 and 100 mg/L) Au(I). The final point to note was the importance of using

high grade acetonitrile, since impurities can affect the chromatographic behaviour of the gold.

3.3.2 Behaviour of the Gold Thiosulfate Complex in the Presence of Additional Sample Thiosulfate

The next step in this study was to examine the effect of matrix ions on the behaviour of gold thiosulfate, in particular those ions that are expected to be present in the leach solutions at appreciable concentrations. Firstly, the effect of thiosulfate, which has already been shown to influence the gold complex when added to the eluent, was examined in detail.

3.3.2.1 Preliminary Experiments

Preliminary studies of thiosulfate matrices indicated a significant variation in the observed gold peak area with the concentration of thiosulfate in the sample. This was examined systematically by injecting a series of gold thiosulfate standards, all containing the same amount of gold, but differing amounts of thiosulfate. The results for thiosulfate concentrations between 0-5 mM in an eluent not containing thiosulfate are detailed in Fig. 3.8 (a). The addition of small amounts of thiosulfate to the sample seemed to exert a similar effect to adding it to the eluent, in that the gold peak area increased concomitantly with thiosulfate concentration in the sample, although a plateau was reached at ~0.5 mM. Note the anomalous result observed for the sample containing 0.1 mM thiosulfate, which was significantly outside the trend observed for the remainder. The injections of this sample followed the injection of a gold check standard containing no matrix ions. This result suggested that a matrix memory effect occurred. Further evidence for

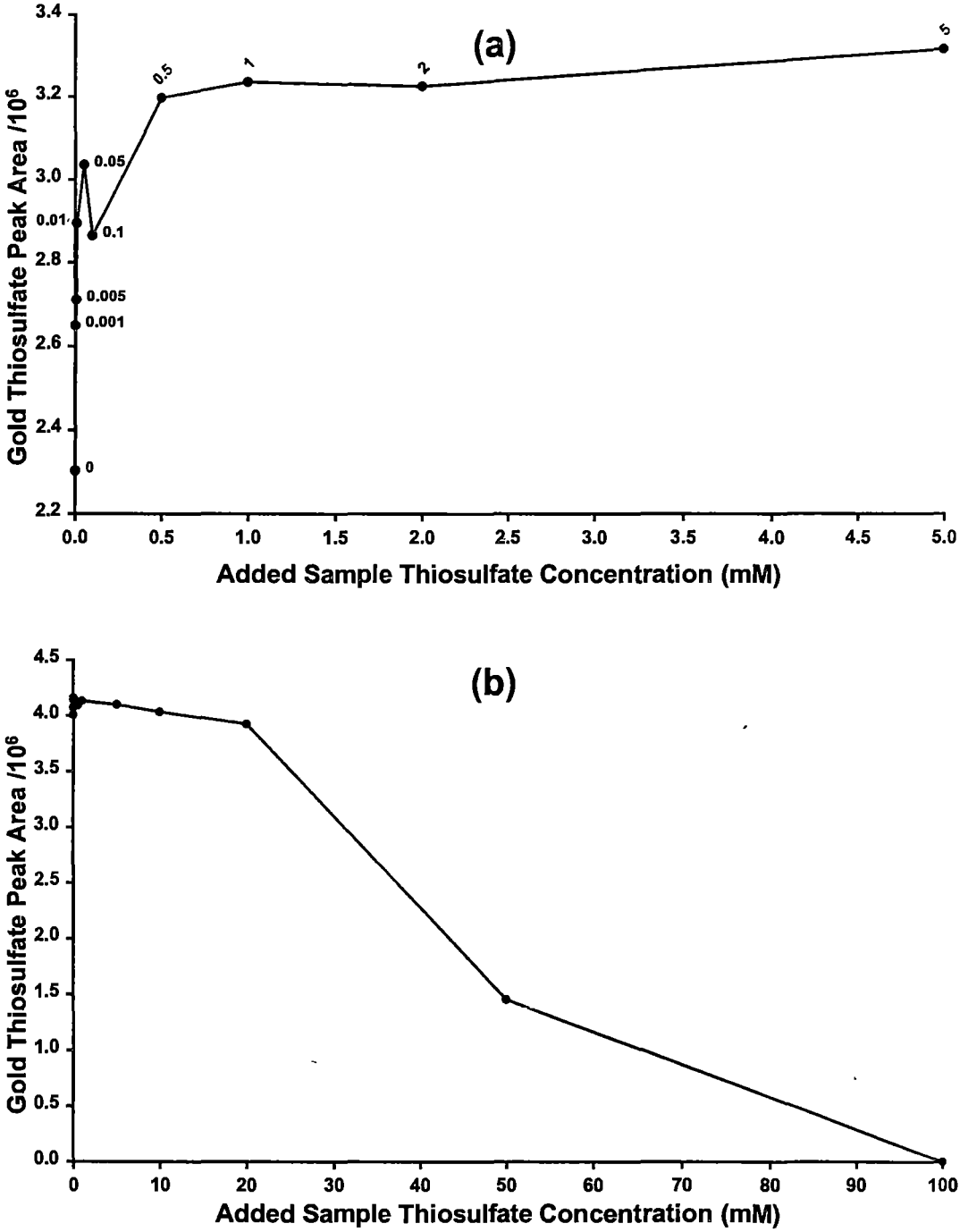

Fig. 3.8 Effect of sample thiosulfate concentration on the gold thiosulfate peak area for a 0.101 mM (19.9mg/L) Au(I) solution, **(a)** between 0-5 mM in an eluent containing no thiosulfate (using (I)) and **(b)** between 0-100 mM using conditions (II).

this was that replicate injections of standards containing no or very low levels (< 10 μM) of thiosulfate showed progressively larger peak areas.

To further test this memory effect theory, triplicate gold standard injections (no matrix ions) were made with single or duplicate injections of water or 1 mM thiosulfate between each gold sample (chromatographic system (I) used). Higher, more reproducible peak areas were obtained for the 3 gold injections when 1 mM thiosulfate was used, adding further weight to the existence of a memory effect.

Considering these results, the effect of thiosulfate concentration in the sample on the gold peak was re-examined, with thiosulfate added to the eluent in this instance, to assess whether this improved the robustness of the gold peak area. For this experiment, much higher concentrations of thiosulfate in the sample (up to 100 mM) were also investigated. The results of this study using an eluent containing 40 μM thiosulfate are shown in Fig. 3.8(b). For samples containing low thiosulfate concentrations, a major improvement in peak area reproducibility was observed between solutions containing different concentrations of thiosulfate. In contrast, for samples containing high concentrations of thiosulfate (> ~5mM) the gold peak area dropped off markedly, with quantitation in the 100 mM thiosulfate standard not being possible since only a raised baseline was observed, as shown in Fig. 3.9. The trend was the same for both conductivity and UV detection. This was obviously of great concern, since leach thiosulfate concentrations are likely to be in the range 0.05-0.5 M, which from the above results may preclude the determination of gold by this technique. Dilution will usually not be possible since this would normally decrease the concentration of

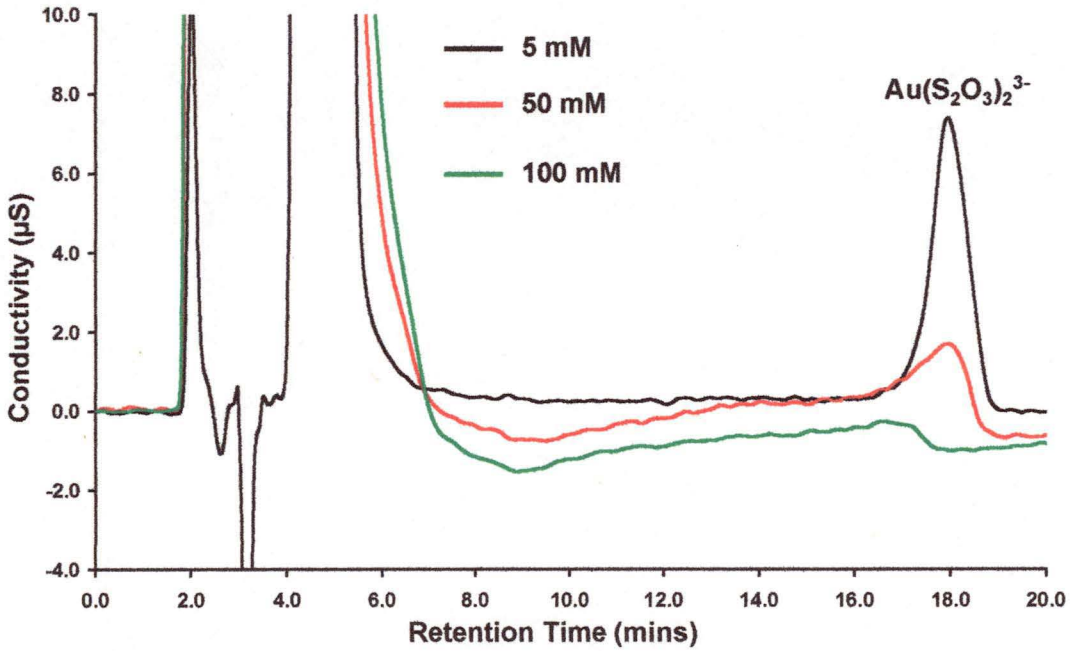

Fig. 3.9 Influence of sample thiosulfate on the gold thiosulfate peak shape. Gold concentration of samples: 0.101 mM (19.9 mg/L). Conditions: (II).

the gold in the sample below the method detection limit, which was determined to be 0.036 mM (7 mg/L as Au(I)), with no additional thiosulfate added to the sample, IC conditions (II)). Even if detection was possible, the actual measured gold concentration would be dependent on the sample thiosulfate concentration. It was therefore important to further investigate the effect of matrices containing high thiosulfate concentrations.

3.3.2.2 High Thiosulfate Matrices

A logical explanation for the reduction in the gold peak area for samples containing high thiosulfate concentrations is the presence of a self-elution effect caused by the ionic strength of this matrix. For such a situation, an experiment keeping the mass of gold injected constant, but with increasing thiosulfate would be expected to demonstrate some peak broadening, and decreased retention of the gold complex. This was tested by injecting a series of standards, all with the same thiosulfate concentration but each with a different gold concentration, with the injection volume set so that the same number of moles of gold would be injected each time. The results (Fig. 3.10) show that broadening of the gold peak did occur as the injection volume increased, but the end of the gold peak occurred at the same time in the chromatogram regardless of the moles of thiosulfate present in the sample. However, comparison with the results from the investigation detailed in Fig. 3.9 showed that the retention factor for the end of the gold peak was not independent of the thiosulfate concentration in the sample. This can be observed by comparing the 100 μL injection of Fig. 3.10 (green chromatogram) to the 0.1 M thiosulfate containing injection in Fig. 3.9 (green chromatogram). In the latter chromatogram the end of the gold peak occurs at a substantially lower retention time than for the other samples in the same experiment.. The only differences

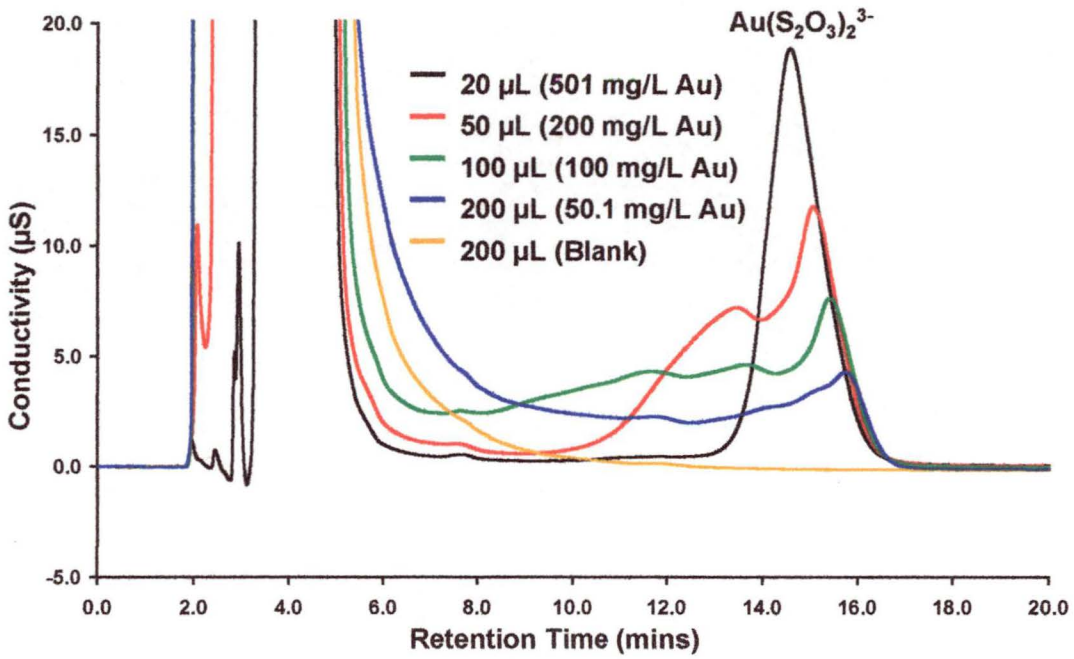

Fig. 3.10 Effect of injecting the same number of moles of gold thiosulfate (5.1×10^{-8} moles), using the specified injection volumes, in standards also containing 0.1 M thiosulfate, on the gold thiosulfate peak shape. Conditions: (I).

between the two chromatograms is that the results in Fig. 3.10 were obtained without the presence of 40 μM thiosulfate in the eluent, and the gold concentration was approximately five times higher than that in Fig. 3.9. This result suggested that the concentration ratio between thiosulfate and gold thiosulfate was important in determining the extent of the broadening effect.

The above results supported the existence of a self-elution effect similar to that described previously by Novic *et al.* [11], for an anion-exchange system employing a sulfate eluent, and samples of nitrate and nitrite containing sulfate as a matrix ion. As the sulfate concentration in the sample was increased, the nitrate and nitrite peaks were observed to broaden towards lower retention times, but the end of the peak did not move. This was attributed to a "sample-induced micro-gradient" in which the higher concentration of the eluting ion in the sample plug caused a lower retention factor for analyte ions contained in that plug, with the effect decreasing from the front to the rear of the sample band, resulting in the observed peak shape.

The results illustrated in Fig. 3.10 were somewhat similar to those described in the above-mentioned work, except the situation here was more complicated. The separation system involved ion-interaction not ion-exchange, the primary matrix ion was different to that contained in the eluent, and the charge on the analyte (-3) was larger in magnitude than that of the eluent (approximately -2).

To understand how the self-elution hypothesis may apply to these samples, consider a sample plug of gold thiosulfate in a matrix consisting of a high

concentration of thiosulfate. Immediately after injection onto the column and before any dispersion of the bands has occurred the band will appear as shown in Fig. 3.11(a). As the plug begins to move down the column the thiosulfate band will start to separate from the gold and a small portion of the gold thiosulfate will be free of the sample plug (b). As the bands continue to move through the column, self-elution from the matrix makes it progressively more difficult for further gold to "escape" the sample band, resulting in broadening of this part of the peak (c), which ceases once the thiosulfate band has completely separated from the gold (d). The end of the peak will always be in the same place according to this mechanism, unless the ionic strength of the matrix is so high that even gold at the end of the band is not immediately free from the sample plug. In addition if position (d) is not reached by the end of the column, some of the sample will be eluted with the matrix ion, as was observed in Fig. 3.10, in the case of the 100 and 200 μL injections. This hypothesis is simplistic with regard to the final shape of the eluted band since the peak shapes observed here are different to those shown in the earlier work by Novic *et al.* [11] However, as noted before the chromatographic system used here was more complicated.

3.3.2.3 Addition of Gold Thiosulfate to the Eluent

As a further assessment of this possible self-elution effect, and also in an attempt to improve the stability of the gold complex on-column, the effect of adding a small amount of the gold thiosulfate complex to the eluent was investigated. IC conditions (II), except with approximately ~0.01 mM Au(I) added as the thiosulfate complex (~2 mg/L Au(I)), were used in this work. There was a substantial increase in peak area corresponding to a gold standard injected in a 1 mM thiosulfate matrix. However, in a sample containing the same gold

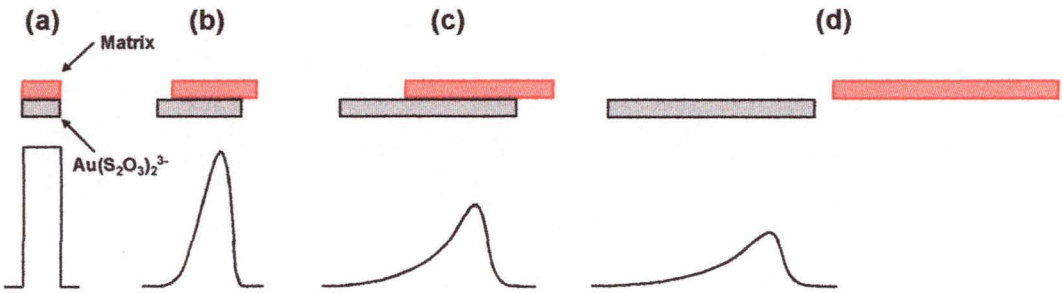

Fig. 3.11 Representation of sample-induced micro-elution hypothesis **(a)** initial state after sample injection **(b)** the gold thiosulfate contained at the end of the sample band "escapes" the sample plug, **(c)** self-elution effects caused by the sample thiosulfate matrix significantly slows the rate at which the remaining gold thiosulfate leaves the sample plug region resulting in significant peak distortion **(d)** gold thiosulfate is completely separated from the sample plug. The plots show how the gold thiosulfate band would appear in the chromatogram at that point (ignoring signal from the matrix).

concentration but 0.1 M thiosulfate, the gold thiosulfate equilibrium in the column was significantly disturbed. A major dip in the baseline (of magnitude ~ 10 μS in the conductivity trace) was observed from the end of the thiosulfate peak until the retention time of the gold thiosulfate complex, where a small peak was observed followed by the recovered baseline. The apparent stripping of the gold thiosulfate complex from the column by the high thiosulfate matrix was consistent with the sample-induced micro-gradient effect. This was because the gold on the column passed by the thiosulfate plug during its passage through the column would experience the same degree of self-elution as the frontmost portion of gold in the original sample plug.

3.3.2.4 Effect of Adding TBAOH to the Sample

Interesting results were obtained when the eluent ion-pair reagent, TBAOH, was added to the sample at a level equal to that contained in the eluent. Samples containing high thiosulfate showed a partial recovery of the gold thiosulfate peak, as illustrated in Fig. 3.12. Samples containing 0.1 M thiosulfate and 3 mM TBAOH produced a peak area for 0.102 mM (~20 mg/L) Au(I) standards which was 85-90% of that for similar standards containing 1 mM thiosulfate. Adding excess TBAOH produced peak area recoveries that were inconsistent between the conductivity and UV detectors (displayed in Fig. 3.13 (a)), the cause of which was unknown. Overall, the results suggested little further improvement in recovery compared to addition of stoichiometric amounts of TBAOH, even for a sample containing the gold thiosulfate complex, 0.1 M thiosulfate and 50 mM TBAOH (over 16 times the level contained in the eluent). The addition of TBAOH to samples containing a low thiosulfate concentration did not significantly influence the gold thiosulfate peak area.

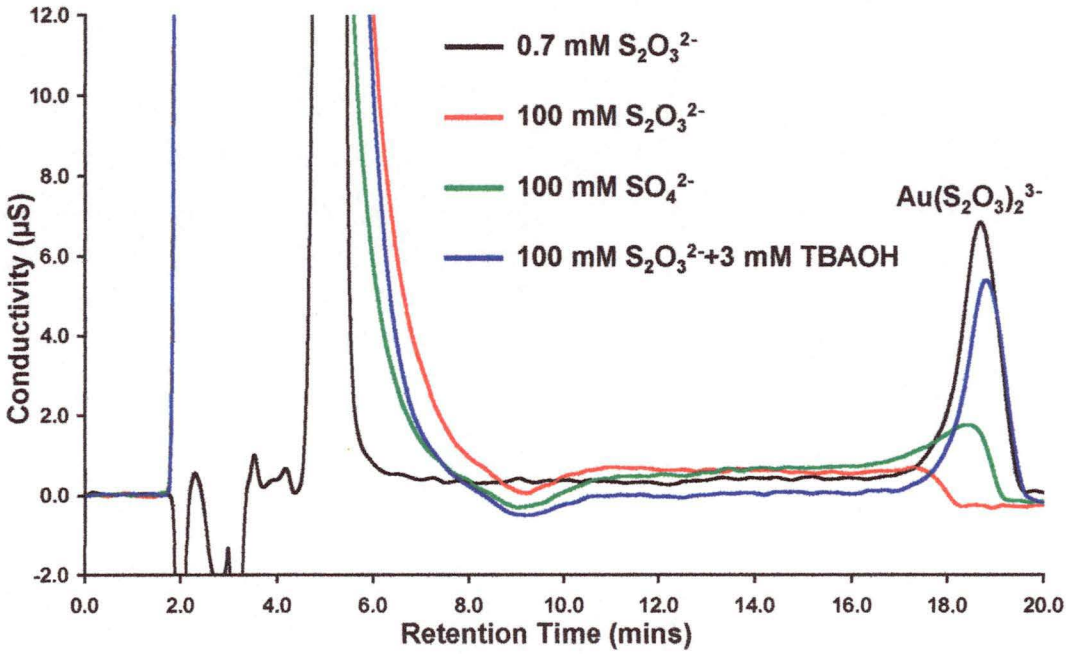

Fig. 3.12 Influence of sample matrix on the gold thiosulfate peak shape. Solutions all contain 0.101 mM (20 mg/L) gold. The peak "recovery" effect of adding TBAOH to the sample can be clearly observed in the presence of a high thiosulfate matrix. Conditions: (II).

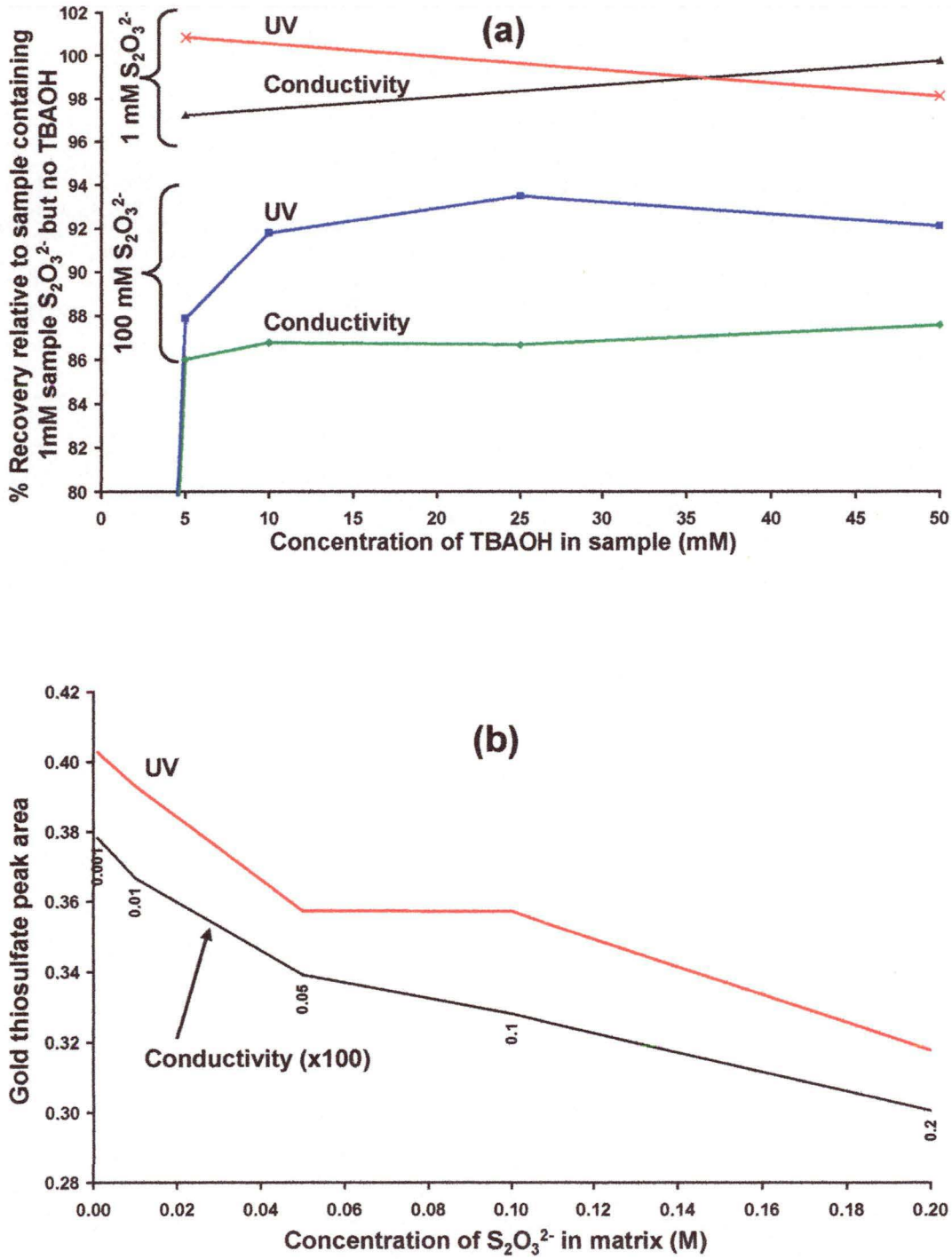

Fig. 3.13 (a) Gold thiosulfate peak area recovery as a function of sample TBAOH concentration, for solutions containing gold at a concentration of 0.103 mM (20.2 mg/L). Recovery based on that obtained for a solution containing 1 mM thiosulfate matrix with no TBAOH present. **(b)** Effect of sample thiosulfate concentration on the gold thiosulfate peak area for solutions containing 0.102 mM (20.0 mg/L) gold and 5 mM TBAOH. Conditions for both (a) and (b): (II).

The behaviour of the gold complex in the presence of sample TBAOH was considered to be a possible means by which the gold thiosulfate chromatography could be stabilised, even if the recovery of the complex through the column was not 100%. Unfortunately a further experiment showed that even with TBAOH present in the sample, the gold thiosulfate peak area decreased with increasing thiosulfate concentration as demonstrated in Fig. 3.13(b), thus preventing the use of this approach.

Despite the above-mentioned problems, the effect of adding the TBAOH to the eluent did provide a further insight into the chromatography of the gold complex in the presence of a high concentration of thiosulfate. The results indicated that the problem with the gold peak was, at least in part, caused by some kind of equilibrium disturbance that occurred with the injection of high-ionic strength samples in the absence of TBAOH.

The reason for the continued loss of some gold peak area even in the presence of TBAOH is unknown, but may in some way still relate to the mechanism hypothesised in the preceding section.

3.3.2.5 Pre-Column Matrix Elimination

Another approach investigated to overcome the problems induced by the thiosulfate matrix utilised methodology similar to that of Haddad and Rochester [5]. This method was an on-line technique utilising a pre-column to remove matrix components and concentrate the gold cyanide complex from cyanide leach liquor waste streams. The main difference was that instead of preconcentration, the aim of the present study was to use the technique to remove

the thiosulfate matrix from the sample, ideally leaving only the gold complex absorbed on the pre-column. The adapted instrumental configuration is described in the experimental section of this chapter. To maximise the difference in retention between thiosulfate and gold thiosulfate, the acetonitrile concentration of the eluent was reduced during the loading step. Preliminary work with a Dionex NG1 column used in the direct injection mode indicated that for an eluent containing 17.5% acetonitrile, 3 mM TBAOH, 2 mM sodium carbonate and 40 μM sodium thiosulfate, a broad gold peak, was eluted at ~20 min, whilst thiosulfate was eluted at ~1.5 min. Unfortunately, experiments in the same configuration using samples containing 0.1 M thiosulfate gave lower peak areas for the gold.

It was of interest to determine if the backflush mode discussed by Haddad and Rochester [5] would recover this gold. For this investigation, a second NG1 column was used as the "analytical" column, to minimise the separation time. A peak for a 0.102 mM (20 mg/L) gold solution was observed in both 1 mM and 0.1 M thiosulfate samples, but in the latter matrix the peak was broad and misshapen, as illustrated in Fig. 3.14(a), (ii). The results are still an improvement over the direct mode, since in this configuration for a sample containing 0.1 M thiosulfate and 0.102 mM (20 mg/L) gold, only the raised baseline was visible. The poor peak shape in the high thiosulfate matrix was also consistent with the previously stated sample-induced micro-gradient hypothesis, since such an effect would have broadened the gold peak on the pre-column during the loading step, producing results similar to those observed in Fig. 3.14(a) (ii). In the back-flush step the gold that had moved the greatest extent through the pre-column because

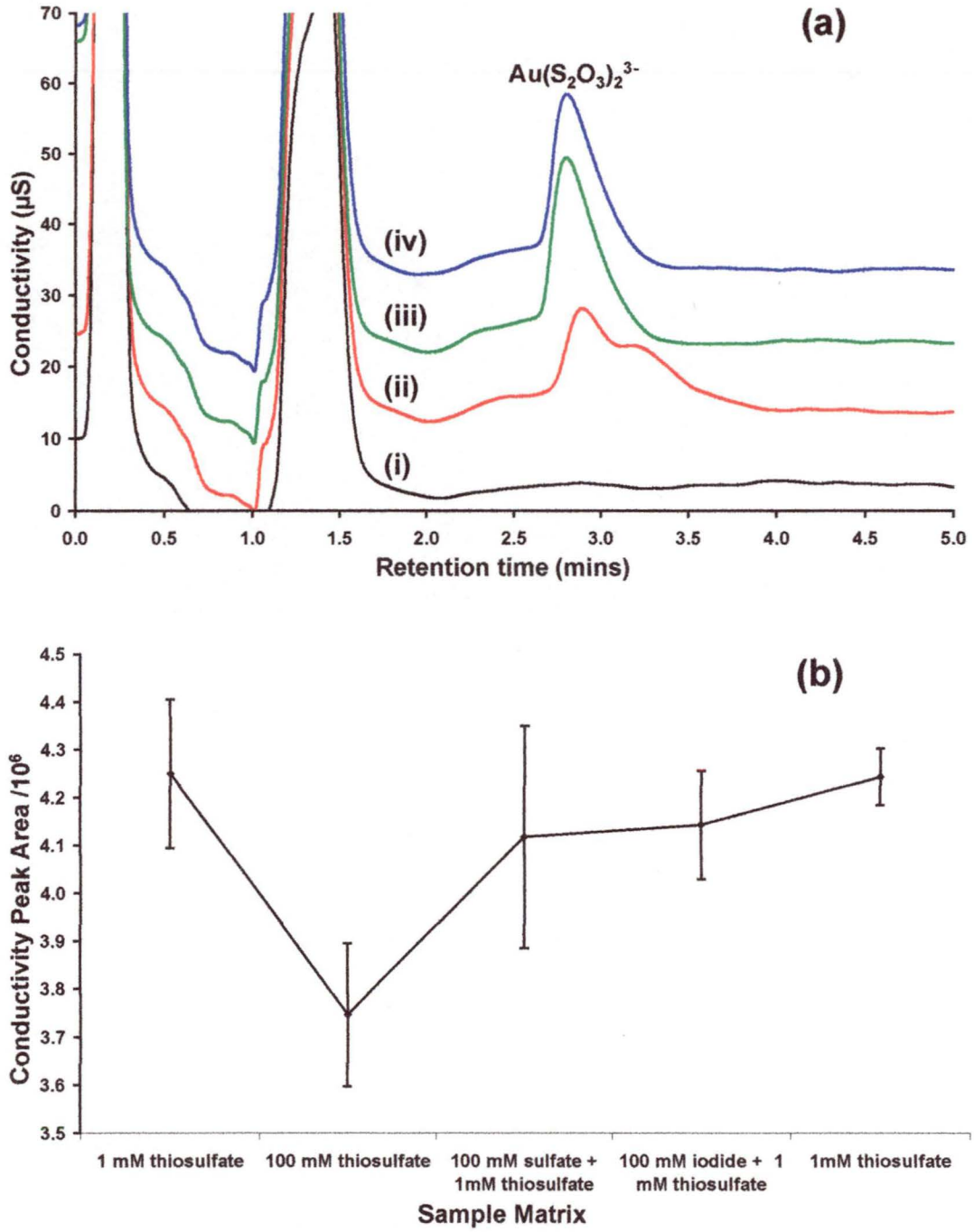

Fig. 3.14 (a) Results of study into the use of a matrix elimination pre-column procedure **(i)** Water Blank **(ii)** 0.101 mM (19.9 mg/L) Au(I) (as thiosulfate) in matrix of 0.1 M thiosulfate **(iii)** 0.101 mM Au(I) (as thiosulfate) in matrix of 1 mM thiosulfate and 3mM TBAOH **(iv)** 0.101mM Au(I) in matrix of 0.1 M thiosulfate and 3 mM TBAOH. **(b)** Effect of sample matrix on resulting gold thiosulfate peak when using a matrix elimination pre-column system, with all samples containing 3 mM TBAOH. Instrumental set-up and program for both (a) and (b) given in experimental section. Matrix elimination step eluent: 17.5% *v/v* acetonitrile containing 3 mM TBAOH 2 mM Na_2CO_3, backflush and analytical eluent: 28% *v/v* acetonitrile containing 3 mM TBAOH 2 mM Na_2CO_3.

of the matrix, although in contact with the stronger analytical eluent first, would still take significantly longer to reach the detector than the portion of the gold absorbed at the head of the column.

The addition of TBAOH to the sample solved this problem, with gold thiosulfate peak area recoveries of between 90-95%, compared to that of a similar sample containing only 1 mM thiosulfate injected in the same system (Fig. 3.14 (a), (iii) and (iv)). The higher recovery may indicate an improvement over the direct injection technique or could also relate to the much shorter column used, which would minimise the effects of any other possible sources of loss of gold in the system.

As a further test, the effect of the matrix ions sulfate, thiosulfate and iodide were compared in this system with TBAOH added to the sample. The eluting strength of these ions is sulfate < thiosulfate < iodide. If the self-elution effect was the cause of the remaining loss in gold thiosulfate peak area, then samples prepared in these matrices should show increasing reduction in the gold peak area with increasing eluting strength of the matrix ion. This was not observed, with iodide showing greater recoveries than thiosulfate, (Fig. 3.14(b)). This result suggested that the remaining loss in gold peak area was not through a self-elution effect, although the high irreproducibility of the data presented a problem for drawing any firm conclusions from these experiments.

3.3.2.6 Investigation of a Zirconia-Based Column

To further assess the role (if any) of the stationary phase substrate on the chromatography of the gold thiosulfate complex, an investigation was conducted

using a zirconia-based column. The advantage of this column over the silica-based material discussed in Section 3.3.1.3 was that the column is stable over a wider pH range, enabling the use of an eluent system similar to that possible on polymer-based columns.

The column used was a ZirChrom Diamond bond C_{18} with 3 μm particle and 300Å pore size. Initial testing indicated that to attain significant retention a lower acetonitrile concentration (15% versus 28% *v/v*) in the eluent was required. The results obtained on this column contrasted markedly with the polymer column, with no significant raised baseline observed by conductivity, and a much reduced raised baseline observed on the UV detector. However, the peak for the gold thiosulfate complex was tailed and/or split, even though thiosulfate was added to the eluent. This behaviour is demonstrated in Fig. 3.15 (a) and (b). Peak area was still influenced by the thiosulfate concentration of the sample, although this effect was not as strong as on the polymer column. For example, a peak was observed for gold in a 0.102 mM (20 mg/L) Au(I) (as thiosulfate) standard containing 0.2 M thiosulfate (Fig. 3.15(b)(iii)), even without TBAOH in the sample. The addition of TBAOH to the sample was actually detrimental to the chromatography of the gold, resulting in smaller peak areas in samples containing high levels of thiosulfate. The retention time of the gold complex also decreased with increasing thiosulfate, although the peak shape of the gold actually improved in a high thiosulfate matrix. The baseline on this column was also more sensitive to high thiosulfate matrices, as is evident from the baseline drift after the thiosulfate peak in Fig. 3.15(b).

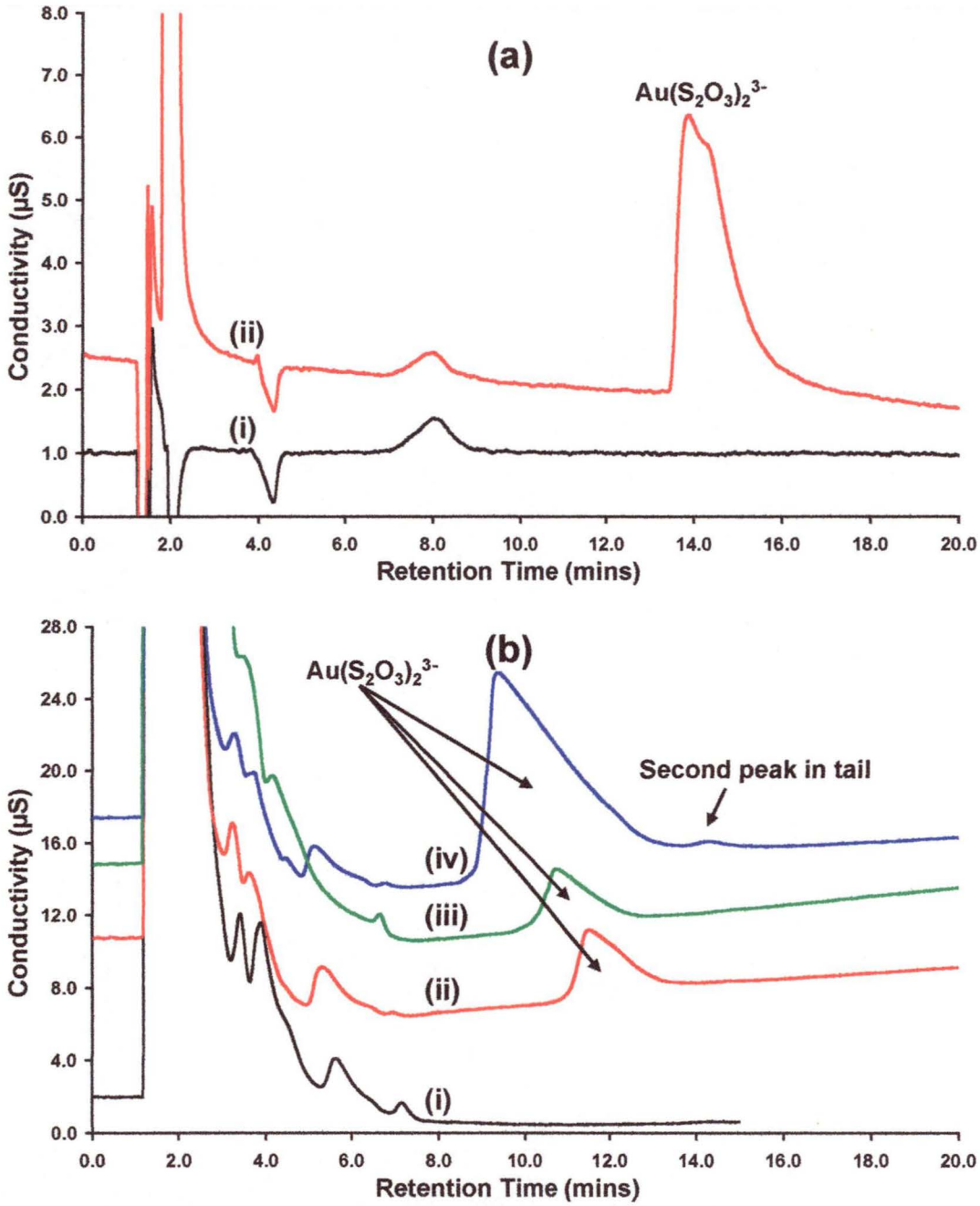

Fig. 3.15 Results from investigations on a Zirchrom DiamondBond C_{18} zirconia based column **(a) (i)** Water Blank **(ii)** 0.102 mM (20.0 mg/L) Au(I) as thiosulfate complex in 1mM thiosulfate matrix **(b) (i)** 0.1 M thiosulfate blank **(ii)** 0.102 mM Au(I) as thiosulfate complex in 0.1 M thiosulfate **(iii)** 0.102 mM Au(I) as thiosulfate complex in 0.2 M thiosulfate **(iv)** 0.509 mM (100.3 mg/L) Au(I) as thiosulfate complex in 0.1 M thiosulfate. Eluent: 15 % *v/v* acetonitrile containing 3 mM TBAOH 2 mM $NaCO_3$ 40 µM $Na_2S_2O_3$.

The detection limit for the gold thiosulfate complex in a 0.1 M thiosulfate matrix was 4 μM (0.7 mg/L Au) by conductivity using this method based on a signal three times the baseline noise, significantly lower than was observed with the polymer-column. In the same matrix, calibration plots between 0.0508 and 0.508 mM (10 and 100 mg/L) Au(I) were linear (R^2> 0.998) for both conductivity and UV detection systems.

Because of the tailed peak shapes and peak splitting effects, this column was not considered further. The markedly different chromatographic behaviour of the gold complex on this column would indicate that the stationary phase does have some role in the separation.

3.3.2.7 Experiments to Determine the Fate of the Gold in High Thiosulfate Matrices

Efforts were made to determine spectroscopically the fate of the gold in samples containing high levels of thiosulfate. The observed change in the area of the gold peak implied that one or more of the following had occurred in the presence of the high thiosulfate matrix:

(a) Precipitation of gold in the sample due to the high thiosulfate matrix prior to chromatographic analysis. This was considered unlikely since there was no visible solid observed in samples and there is no information in the literature indicating limited solubility of the gold in a thiosulfate matrix.

(b) Gold was eluted earlier in the chromatogram than the main gold peak due to a self-elution or other effect. Significant evidence has already been presented to

suggest that this may be a significant factor in the chromatography of gold thiosulfate.

(c) Some of the gold was eluted later than the gold peak due to formation of more highly retained complexes. For example it may be possible that $Au(S_2O_3)_3^{5-}$ was formed in the high thiosulfate matrix.

(d) Gold was precipitated on the column.

(e) The elution behaviour of the gold was the same as in the absence of matrix ions, but the detected form has changed. This theory seems unlikely since the retention time of the gold peak remains unchanged, and the loss in peak area in the presence of high levels of thiosulfate was similar for both the conductivity and UV traces, suggesting that the detected species was the same in both situations.

To test theory (a), solutions containing 0.203 mM (40.1 mg/L) of the gold complex were analysed by flame AAS in a matrix of 1 mM thiosulfate and 0.5 M thiosulfate. The results indicated no significant difference in absorptivities, although dilution (1:5) of the 0.5 M thiosulfate solution was required since the high ionic strength of the matrix caused some suppression of the gold signal. The results suggested that pre-chromatographic precipitation was not a source for loss of the gold.

To investigate mechanisms (b)-(e), column fractions collected from injections of various gold thiosulfate solutions, using IC conditions (II), were analysed by GF-AAS. As noted earlier in this chapter, there were significant difficulties in obtaining quantitative results by this technique. A range of conditions were used

for the GF-AAS determination, mainly to overcome problems caused by the high acetonitrile content of the column eluate which often resulted in a portion of the sample "creeping" up the sides and out of the top of the furnace. It proved necessary to dilute the solutions containing 28% acetonitrile with water (1:2), to reliably prevent this effect. Whilst linear calibration curves were attained for both gold chloride AAS standards and for gold thiosulfate standards prepared in the eluent matrix, quantitation of the collected fractions was not possible since all experiments produced extremely high recoveries. To ensure this effect was not related to the presence of gold on the column that was remobilised in later injections, fractions from the first injection of the gold complex on a new column were analysed, but again high recoveries were obtained. Similar results were observed on the same column after 22 injections of a ~0.102 mM (~20 mg/L) Au(I) solution in 0.1 M thiosulfate and 3 mM TBAOH. As a result, all these investigations were inconclusive.

In view of the inconsistencies observed using GF-AAS, flame methodology was also examined. Recoveries determined using this technique were also high, with injections of a 0.508 mM (100 mg/L) gold standard in the absence of any matrix ions (using IC method (III)) producing gold recoveries typically between 110-120%. However, this error was considered to be within the accuracy limitations of the experimental methodology. Injections of a 0.508 mM gold standard in a 0.5 M thiosulfate matrix (no TBAOH added) showed the presence of some gold in the fraction eluted immediately before that containing the main gold peak (Fig.3.16(a)), which was not observed for a 0.508 mM gold standard without the matrix ion (Fig. 3.16(b)). It should be noted that this behaviour was also evident in

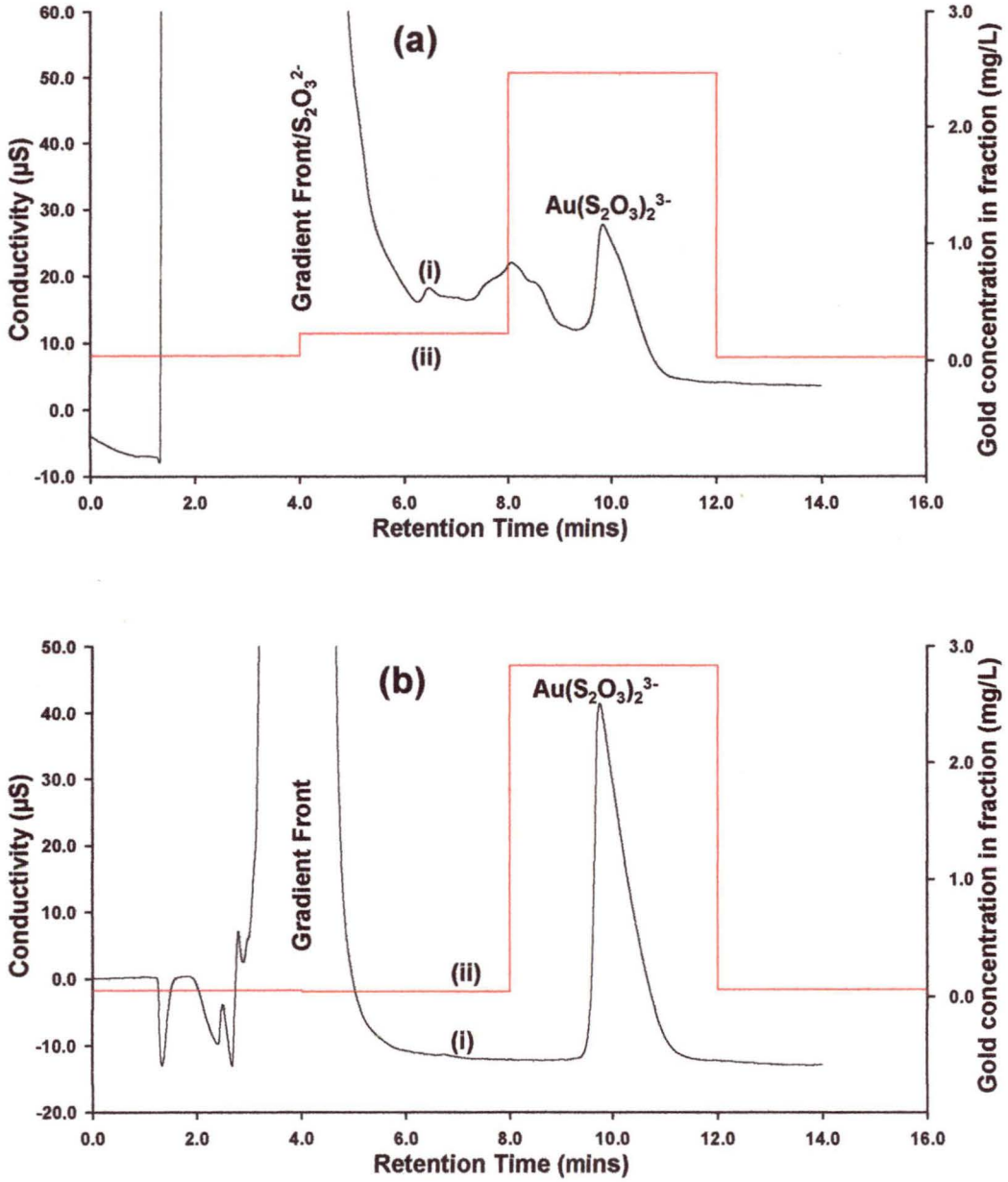

Fig. 3.16 Influence of matrix thiosulfate on the gold distribution in corresponding separations, determined by flame AAS. Samples: **(a)** 0.508 mM Au(I) (as thiosulfate complex) with 0.5 M thiosulfate present **(b)**. 0.508 mM (100 mg/L) Au(I) (as thiosulfate complex) with no matrix. For each Fig. **(i)** is the chromatogram resulting from injection of the relevant sample and **(ii)** is the gold concentration found in each fraction collected. Conditions: (III).

the corresponding chromatograms, with broadening of the gold peak in samples containing high levels of thiosulfate. These observations were consistent with the sample-induced micro-gradient mechanism discussed previously.

3.3.3 Chromatography of the Gold Thiosulfate Complex in the Presence of Matrix Ions other than Thiosulfate

3.3.3.1 Ammonia

The concentration of ammonia in thiosulfate leach solutions is often very high and extremes between 0.1-6 M have been reported [12]. In the absence of additional thiosulfate it was also hypothesised that the gold thiosulfate complex could convert to the gold ammine ($Au(NH_3)_2^+$) species. As a result, the effect of a 1 M ammonia matrix on the chromatography of the gold thiosulfate complex was investigated. There was no significant change in the chromatographic behaviour from a similar standard containing no ammonia. This result provided further evidence that the degree of formation of the gold ammine complex is insignificant under gold thiosulfate leach conditions.

3.3.3.2 Polythionates

The only polythionates that are likely to be in the leach at an appreciable concentration are trithionate and tetrathionate. The presence of these ions in the sample matrix had a detrimental effect on the chromatography of the gold, as evidenced by Fig. 3.17(a), (ii) and (iii). In this system the separation selectivity had been adjusted so that the gold peak was eluted later than tri-, tetra- and pentathionate. Flame AAS investigations on standards containing 0.508 mM (100 mg/L) gold and 2 mM of either trithionate or tetrathionate (using IC system (III)) showed a lower gold recovery in the case of trithionate (~100% compared with

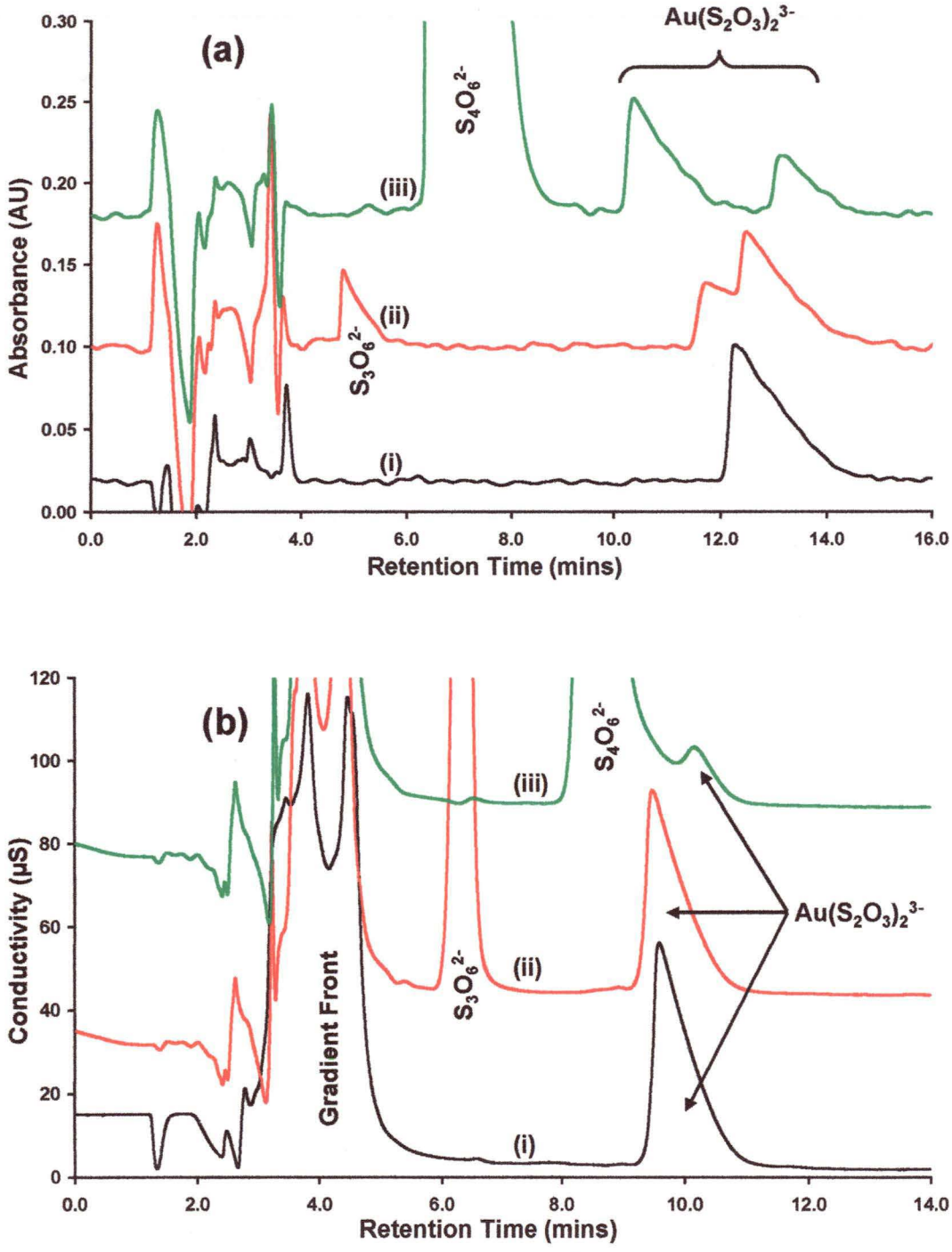

Fig. 3.17 Influence of polythionates on the behaviour of the gold thiosulfate peak. **(a)** **(i)** 0.203 mM (40 mg/L) Au(I) (as thiosulfate complex) **(ii)** 0.203 mM Au(I) (as thiosulfate complex) + 2 mM $S_3O_6^{2-}$ **(iii)** 0.203 mM Au(I) (as thiosulfate complex) + 2 mM $S_4O_6^{2-}$. Conditions: Dionex NG1+NS1-5µ in series 30% *v/v* acetonitrile 3 mM TBAOH 0.5 mM Na_2CO_3 40 µM $Na_2S_2O_3$, UV detection at 215 nm. Conditions chosen so that the gold eluted after the polythionate ions. $S_2O_3^{2-}$ **(b)** Chromatogram identities the same as **(a)** except this time with 0.506 mM (99.7 mg/L) Au(I) in each sample. Conditions: (III).

110-120% for standards in the absence of matrix ions), whilst the recovery was unchanged in the tetrathionate solution. However, there was significant broadening of the gold peak, in the tetrathionate matrix (Fig. 3.17(b) (iii)). The specific cause of the results is unknown, although it may relate to the equilibrium between thiosulfate and the polythionates shown in Eqn. 1.14 (Section 1.6.2), or alternatively to the sample-induced micro-gradient effect discussed earlier. The latter theory is possible since it would be expected that much lower concentrations of these ions would be required than thiosulfate for self-elution to occur, because of their higher ion-exchange affinities. As noted in Chapter 1, polythionates present a problem for gold thiosulfate leaching because of their ability to elute gold from ion-exchange recovery systems [13,14].

These results all demonstrated that major impediments existed in the determination of the gold. For example, even if a successful matrix elimination system as discussed in Section 3.3.2.5, was developed to remove thiosulfate from the sample, removal of polythionates (especially tetrathionate) from the system would be difficult due to the similarities of their ion-exchange affinities to that of the gold complex.

3.4 Conclusions

This study on the ion-chromatographic behaviour of the gold thiosulfate complex, primarily using the Dionex NS1 stationary phase dynamically coated with TBAOH as ion-interaction reagent, has revealed many problems that hinder the determination of this species. In solutions containing no matrix ions, a raised baseline was observed which was partially attributed to on-column dissociation of the complex. This effect could be minimised (but not eliminated) by adding a

small amount of thiosulfate to the eluent. Other mechanisms that could explain this behaviour were not elucidated, but some investigations suggested that on-column precipitation of a portion of the gold occurred during the separation. The purity of the acetonitrile used for the chromatographic analysis was also significant

Addition of other matrix ions, such as thiosulfate or polythionates, introduced further problems in the chromatographic determination of the gold complex. The area of the gold peak was highly dependent on the thiosulfate concentration in the sample and memory effects were significant. For samples containing low-levels of thiosulfate, peak area reproducibility and dependence on thiosulfate concentration could be minimised by the addition of thiosulfate to the eluent. This approach was not successful for samples containing high concentrations of thiosulfate, for which the gold peak area was reduced, and a peak broadening effect was often observed. The results suggested that these problems were at least in part due to a sample-induced micro-gradient effect, for which further evidence was observed in experiments using a matrix-elimination pre-column with back-flush procedure. Spectroscopic studies were also consistent with a self-elution effect.

Adding TBAOH to the sample at a concentration equal to that of the eluent was found to improve significantly the recovery of the gold thiosulfate peak for samples containing high concentrations of thiosulfate. The result indicated that at least a significant portion of the problems observed in the high thiosulfate matrix were caused by disturbances to the equilibrium on the column in the region of the sample plug.

The self-elution effects might not be the only mechanism at work since the chromatographic behaviour of the gold complex was somewhat different on a zirconia-based stationary phase. With this stationary phase, no peak broadening effects were observed and the addition of TBAOH to the sample was detrimental to the chromatography in the presence of a high thiosulfate matrix.

The negligible change in behaviour of the gold complex in the presence or absence of a high ammonia matrix adds further weight to other experimental data in the literature [12] that the gold ammine complex, $Au(NH_3)_2^+$, will not be a significant species in leach solutions, at least at room temperature.

The results outlined in this chapter demonstrate the complexity of applying IC to the quantification of the gold thiosulfate complex. Chapter 4 will continue this investigation, optimising the separation of the gold complex and the polythionates and observing the behaviour of the gold complex in the presence of synthetic leach matrices.

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Chapter 4

Separation of Polythionates and the Gold Thiosulfate Complex in Gold Thiosulfate Leach Solutions by Ion-Interaction Chromatography

4.1 Introduction

As discussed in Chapter 1, the polythionates are important species in thiosulfate leach solutions, with monitoring being required to both aid in understanding and optimisation of the leaching process, and because of their role as competing ions in ion-exchange gold recovery systems. Existing literature on determination of these ions in leach solutions is quite limited, with only four papers [1-4] referring to determinations of at least one polythionate in leach solutions, of which only two provide any experimental detail. Both of these determine thiosulfate simultaneously with the polythionate ions which suggests that a significant dilution factor is required prior to analysis. As noted previously this may induce speciation changes in the mixture. Because of this, a system which requires no, or at most minimal, dilution would be an advantage.

This chapter describes the development of an ion-interaction method for the determination of polythionates in gold thiosulfate leach solutions, with the system being optimised for the separation of the first three polythionates ($S_xO_6^{2-}$ x =3 to 5) and the gold thiosulfate complex. Also, investigations into the behaviour of the gold thiosulfate complex begun in the previous chapter are concluded, with experiments being conducted on the effect of the leach matrix on the

chromatography of this ion. Finally, the effectiveness of the developed methodology for the determination of polythionates in undiluted leach solutions is investigated.

4.2 Experimental

4.2.1 Instrumentation and Reagents

The ion-chromatograph and AAS used in this work was as described in the relevant sections of Chapter 3 (Sections 3.2.1 and 3.2.3). For the study of copper elution in the optimised system, a post column reaction (PCR) system was added. A Model 350 HPLC pump (Scientific Systems Inc., State College, PA, USA) was used to deliver the PCR reagent at a flow rate of 1 mL/min. The reagent was based on that used by Shaw *et al.*[5] and contained 0.5 mM 4-(2-pyridylazo)resorcinol monosodium salt hydrate (PAR), 2.6 M ammonia and 0.85 M ammonium nitrate. A Teflon mixing tea followed by a reaction coil (150 cm x 0.3 mm I. D.) between the column and the detector connected the PCR system to the flow path of the IC. A detection wavelength of 510 nm was used to detect the copper-PAR complex.

The columns used throughout this work were a Dionex NG1 and NS1-5µm in series unless otherwise specified. Peak identifications were determined from the injection of standards of each analyte.

4.3 Results and Discussion

4.3.1 Optimisation of Separation Conditions

The literature review showed that one of the most common IC systems employed for the separation of polythionates is the use of ion-interaction chromatography

employing a reversed phase Dionex NS1 column (with NG1 guard), tetrabutylammonium hydroxide (TBAOH) as the ion-interaction reagent, sodium carbonate as the primary eluting ion, and acetonitrile as the organic modifier. It may seem surprising that such an alkaline eluent has been used since it is well documented [6-8] that tetrathionate and pentathionate are unstable at alkaline pH through reaction with the hydroxide ion. However, the rate of decomposition appears to be slow enough to prevent it from hindering the analysis. It can be expected that the use of an alkaline eluent would cause decomposition of a small portion of the injected polythionate as a continuous process on the column, thereby slightly increasing the detection limit. However, this eluent does have the advantage in that it is compatible with both suppressed conductivity and UV detection modes, which is useful since trithionate has a weak UV chromophore [9] and is more suited to detection by conductivity, while UV detection is more sensitive for tetra- and pentathionate [9].

Preliminary work, combined with evaluation of the previous literature, suggested that the dominant factors in the separation process were the acetonitrile and carbonate concentrations of the eluent. It was therefore decided to optimise the eluent using these parameters, keeping the TBAOH concentration of the eluent constant at 3 mM, since this was found suitable to maintain a stable dynamic loading on the column. In addition, it was found that when using isocratic eluents, the trithionate appeared as a split peak under conditions for which the other ions of interest were eluted quickly. To resolve this problem it was necessary to insert an acetonitrile step gradient from 15% to the higher "separation" concentration during the analysis, which will be discussed later.

The UV spectra of the polythionates are known, with λ_{max} values of < 200 nm for trithionate and between 210-220 nm for tetra- and pentathionate [9]. The absorption spectrum (over the region 200-600 nm) of the gold thiosulfate complex, as discussed in Chapter 3, (Section 3.3.1.1, Fig. 3.3), showed an absorbance maximum at ~205 nm, although in view of the additional baseline noise observed at this and lower wavelengths, 215 nm was used for this work to achieve an improved signal to noise ratio.

Figs. 4.1(a) and (b) demonstrate the effect of acetonitrile and carbonate concentrations on the separation. Acetonitrile provides no means of changing the separation selectivity, but affects the analyte retention by influencing the amount of adsorbed TBAOH on the stationary phase. On the other hand, the carbonate concentration strongly influences the selectivity for the gold thiosulfate complex with retention orders of $Au(S_2O_3)_2^{3-} > S_5O_6^{2-} > S_4O_6^{2-} > S_3O_6^{2-}$ being observed when no carbonate is present and $S_5O_6^{2-} > S_4O_6^{2-} > Au(S_2O_3)_2^{3-} > S_3O_6^{2-}$ at 10 mM carbonate. This effect can be explained by the higher charge (-3) on the gold thiosulfate complex compared to the polythionates (-2), indicating that the gold thiosulfate complex will be more strongly influenced by eluent concentration [10]. This ability to move the gold thiosulfate peak relative to the peaks for the polythionates is advantageous since it can be used to decrease interferences when required.

Based on the results from this study, and with the gradient step time set to occur at injection, the optimum eluent was determined to consist of an acetonitrile step

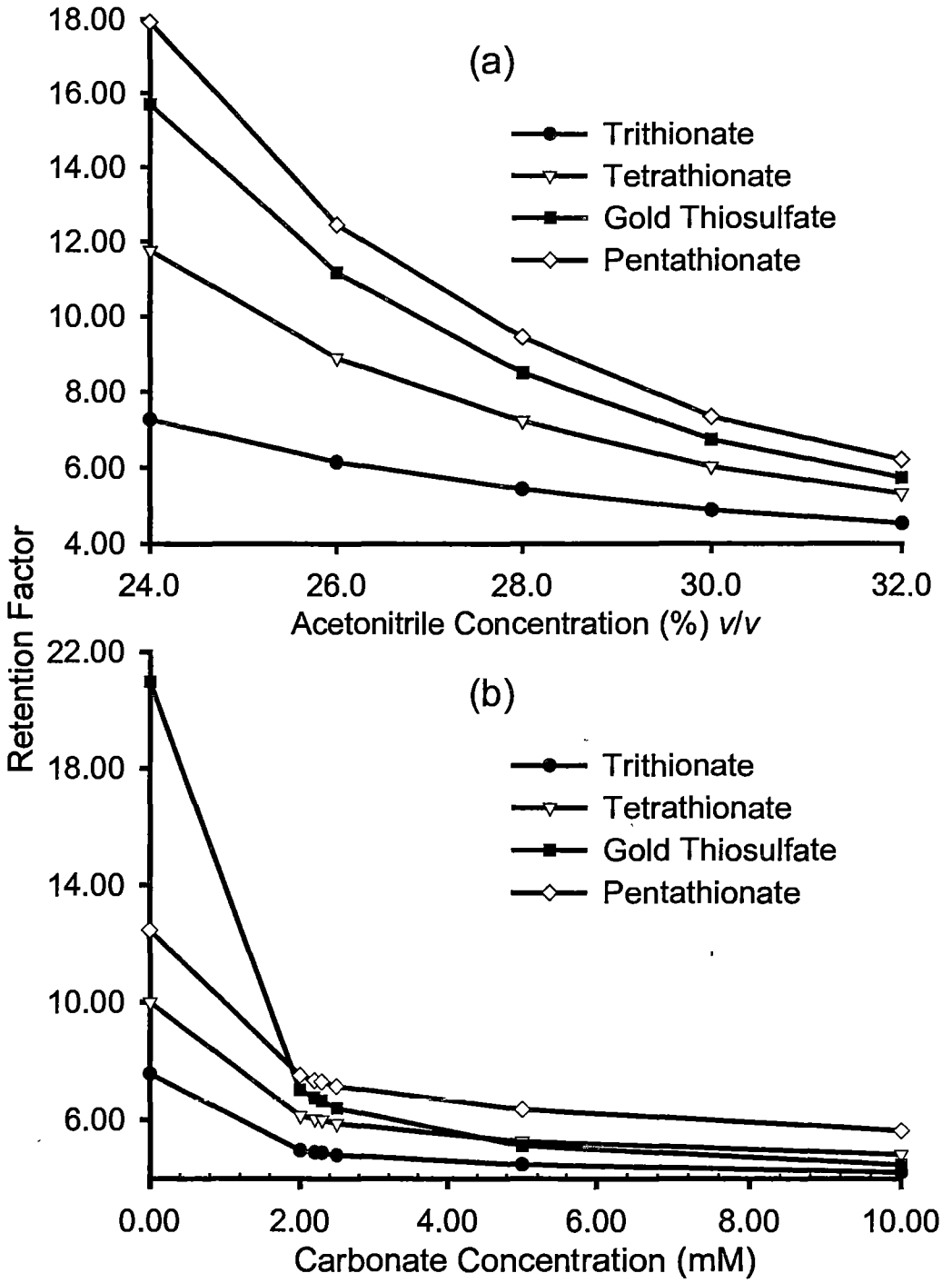

Fig. 4.1 Effect of (a) acetonitrile and (b) carbonate concentrations in the eluent on retention and separation of polythionates and the gold thiosulfate complex. Eluent compositions: (a) 3mM TBAOH, 2.2mM sodium carbonate, acetonitrile step gradient at 2.5 mins from 15% *v/v* to the indicated final composition, (b) 3mM TBAOH, acetonitrile step gradient at 2.5 mins from 15% *v/v* to 30% *v/v*. For remaining conditions, see Sections 3.2.1 and 4.2.1.

gradient from 15% to 28% *v/v*, with 3 mM TBAOH and 2.5 mM sodium carbonate maintained in the eluent at all times. After 14 min, the acetonitrile concentration was reduced to 15% and held for a period of 4 min, yielding a total analysis time of 18 minutes, including the time required to re-equilibrate the column with the initial conditions. The separation attained using this eluent is illustrated in Fig. 4.2 as recorded by both the conductivity and UV detectors. These conditions were chosen so that the gold thiosulfate eluted between tetra- and pentathionate, since the gold thiosulfate peak became extremely tailed with increasing residence time on the column.

4.3.2 Analysis of Synthetic Leach Solutions

A wide range of thiosulfate leach conditions have been reported in the literature [11], varying between the extremes of 0.1-2 M for thiosulfate, 0.1-6 M for ammonia and 0.001-0.1 M for copper. Based on a recent review [11] and our own experience it was concluded that approximately 70% of leaching regimes use $\leq$ 0.5 M thiosulfate, $\leq$ 2 M ammonia and $\leq$ 50 mM copper. In order to ensure the chromatographic method was able to separate species present under realistic leach conditions a synthetic leach solution containing the above concentrations of these species was used. While it is unlikely that these extreme conditions would be used widely in any real leach solution, they provide a very challenging matrix in which to evaluate the method.

4.3.2.1 Gold Thiosulfate Complex Behaviour in the Leach Matrix

From the results discussed in Chapter 3, it was anticipated that the determination of the gold thiosulfate complex would prove difficult. To investigate the effect of such samples, injections of two 0.508 mM (100 mg/L) gold(I) solutions (present

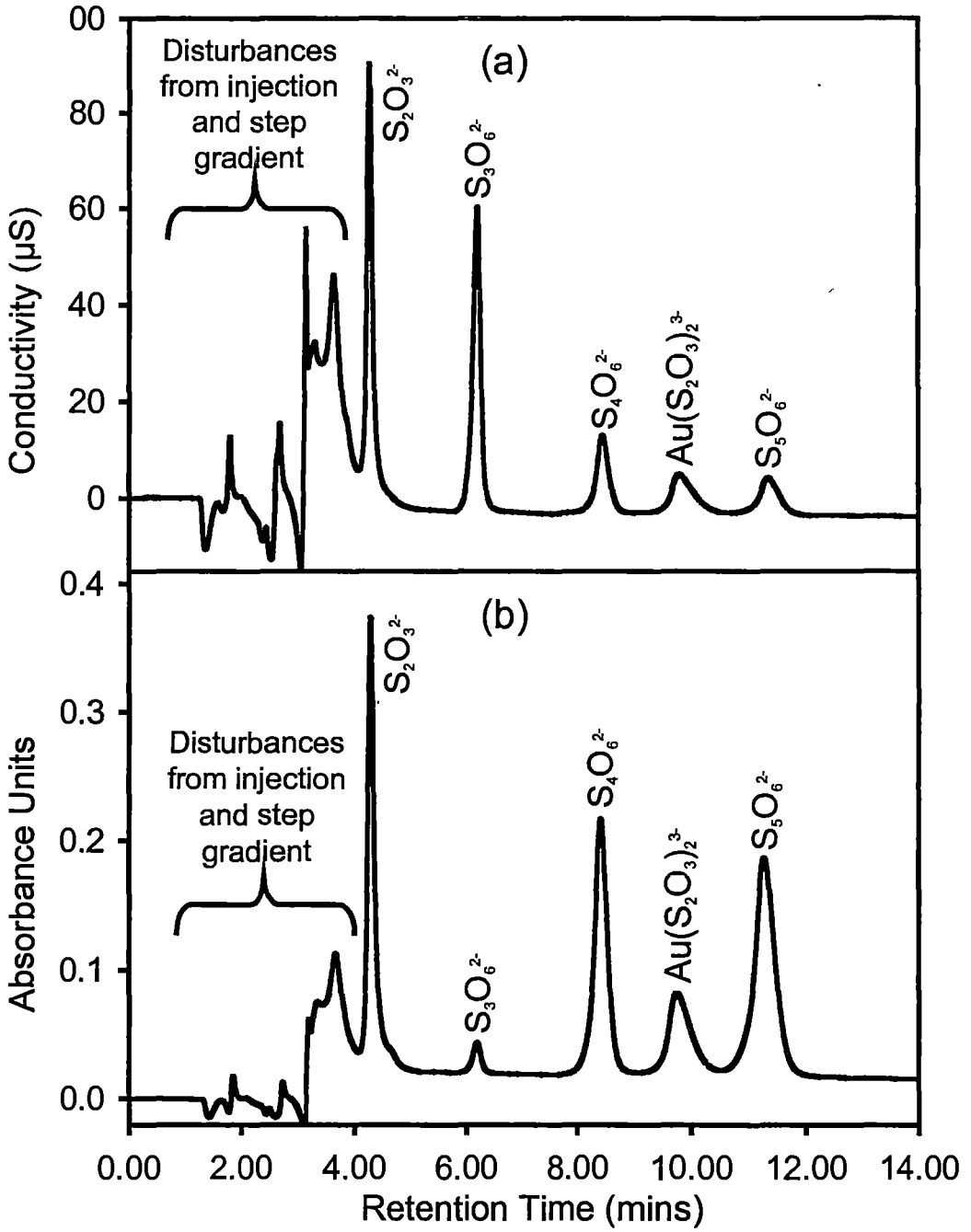

Fig. 4.2 (a) Conductivity and (b) UV chromatograms of optimised separation for the polythionates and gold thiosulfate. Optimum eluent composition, acetonitrile step gradient at 0.0 min from 15% *v/v* to 28% *v/v*, 3 mM TBAOH, 2.5 mM sodium carbonate. Sample composition, (0.18 mM (20 mg/L) thiosulfate, 0.21 mM (40 mg/L) trithionate, 0.094 mM (21 mg/L) tetrathionate, 0.10 mM (20 mg/L) gold (as thiosulfate complex), 0.082 mM (21 mg/L) pentathionate.

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as the thiosulfate complex) were made in the optimised system, one containing and the other free of the leach matrix. The results of the study are shown in Fig. 4.3, with Fig. 4.3(a) detailing chromatograms resulting from 100 μL injections of the (A) leach containing and (B) leach free solutions. Fig 4.3(b) shows another injection of the leach containing sample, except using only a 10 μL injection volume. Note, that for this work (and all other separations discussed in this section), 40 μM thiosulfate was added to the optimised eluent, since earlier work (refer to Chapter 3, Sections 3.3.1.2 and 3.3.2.1) indicated that such an addition assisted in stabilisation of the gold thiosulfate complex. As was previously observed, this caused an increase in baseline noise for both detectors, but did not significantly affect the separation between the gold thiosulfate complex and the polythionates.

Fig 4.3(a) highlights that the gold thiosulfate peak is greatly reduced in leach liquors compared with standards. Results using both the NS1 (10μm) and NS1-5μ columns employing eluents similar to the optimised system described in the previous section (containing no acetonitrile step gradient, and using different carbonate concentrations), showed that adding TBAOH to such samples did not seem to offer the same gold peak recovery properties observed for solutions containing only high thiosulfate (refer to Chapter 3, Section 3.3.2.4).

As a first step in establishing the fate of the gold, the possibility of gold precipitation in the leach solutions prior to chromatographic analysis was considered. A comparison of flame AAS absorbance values obtained for 0.204 mM (40.1 mg/L) of gold(I) in the leach matrix described earlier (also

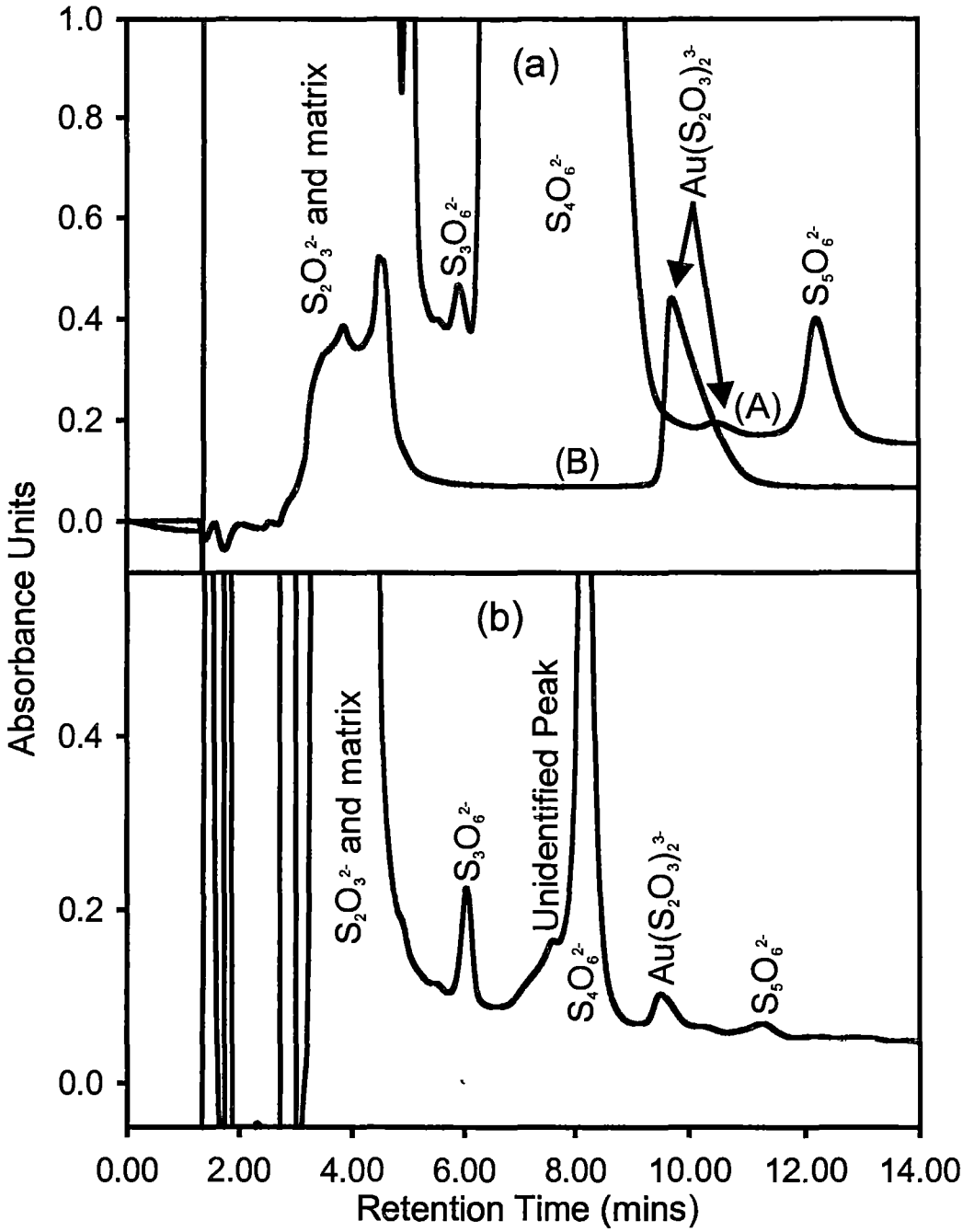

Fig. 4.3 (a) Overlay of UV chromatograms for (A) an artificial leach solution containing 0.5 M ammonium thiosulfate, 2 M ammonia, 0.05 M copper sulfate and 0.508 mM (100 mg/L) gold (as thiosulfate complex) and (B), a 0.508 mM (100 mg/L) gold standard (as thiosulfate complex), using the optimised separation conditions. Injection volume 100 µL. (b) UV chromatogram of the artificial leach solution under the same conditions except using a 10 µL injection volume. The conductivity chromatograms were similar.

containing 3 mM TBAOH from a stock solution that had been adjusted to pH 7 with phosphoric acid) diluted 1:5, was approximately 95% the value obtained in a similarly prepared solution containing only 1 mM thiosulfate (plus the same TBA^+ matrix). The difference is thought to be attributable to signal suppression caused by the high ionic strength matrix. In contrast, analysis of the leach containing sample at the same time by IC, using a 30% *v/v* acetonitrile 3mM TBAOH, 0.5 mM Na_2CO_3 40 μM $Na_2S_2O_3$ eluent (chosen so that the gold was eluted after pentathionate), resulted in no observable gold peak. These results indicated that most, if not all, the gold chromatography problems occur during the chromatographic process.

To determine the fate of the gold on-column, column fractions were collected during the IC analysis of samples containing 0.508 mM (100 mg/L) gold(I) (as the thiosulfate complex) with and without the presence of the leach matrix, using the optimised separation conditions. For each analysis four fractions were collected, corresponding to the 0-4, 4-8, 8-12 and 12-16 min intervals, where t = 0 was the injection time, with the gold concentration determined by AAS. The results of this study are provided in Table 4.1, which shows the average concentration of gold in each fraction and the total average gold recovery for each injection. Theoretically, all the gold should be contained in the 8-12 min fraction (see Fig. 4.3(a)) with a concentration of 12.7 μM (2.5 mg/L Au). Average total gold recovery was high for both the standard (115%) and leach (122%) solutions. As noted for similar studies discussed in Chapter 3 (Section 3.3.2.7), these recoveries are probably within the uncertainty of the experiment. For the leach sample, it appears that the gold was spread across the first three fractions collected,

Table 4.1 Average gold concentrations observed in IC column fractions, and total gold recovery for 100 µL injections of 0.508 mM (100 mg/L) gold thiosulfate standard and artificial leach solutions containing 0.508 mM gold as thiosulfate, measured by AAS [*n* = number of replicates].

Sample	[Au] (µM)				Average total gold recovery (%)
	0-4 min	4-8 min	8-12 min	12-16 min	
0.508 mM gold standard (as thiosulfate complex) [*n* = 2]	0.2	0.2	14.1	0.3	115
Artificial leach spiked with 0.508 mM gold (as thiosulfate complex) [*n* = 3]	2.9	5.23	7.06	0.2	122

consistent with the self-elution effect discussed previously. These results demonstrated that gold thiosulfate cannot be determined in the leach solutions by this method and the species was therefore not considered further. As a result, thiosulfate was not added to the eluent in the remainder of the work discussed in this chapter.

4.3.2.2 Polythionate Chromatography in the Leach Matrix

The only difficulty that the leach matrix provided for the polythionate determination is the unknown shoulder peak on the front of the tetrathionate peak (Fig. 4.3(b)). To determine whether this peak was caused by an anionic copper species, such as $Cu(S_2O_3)_2^{3-}$ or $Cu(S_2O_3)_3^{5-}$, the elution of copper in the system was also examined. A post column reaction system using PAR, followed by visible detection at 510 nm, was used to monitor copper elution in further injections of the artificial leach solution. The results are shown in Fig. 4.4. The retention of copper varied according to the injection volume, with different results being obtained for injections of 10 and 100 µL. In both cases there was a significant peak in the region of the void volume, presumably corresponding to cationic complexes of copper, such as the tetra-ammine copper(II) complex, $Cu(NH_3)_4^{2+}$. However, there was also a diffuse peak observed for the 10 µL injection (Fig. 4(a)) between 3.4-5.0 min, and a small peak at 3.3 min, followed by a large poorly shaped peak between 4.0-5.8 min for the 100 µL injection (Fig. 4.4(b)). These may correspond to the copper thiosulfate species mentioned earlier. Recoveries were not quantitative, since after many injections of leach solutions, flushing the column with 0.5 M ammonia produced a major response from the PCR system, which took some hours to dissipate. For both injection volumes no copper was observed in the region of the shoulder peak and this

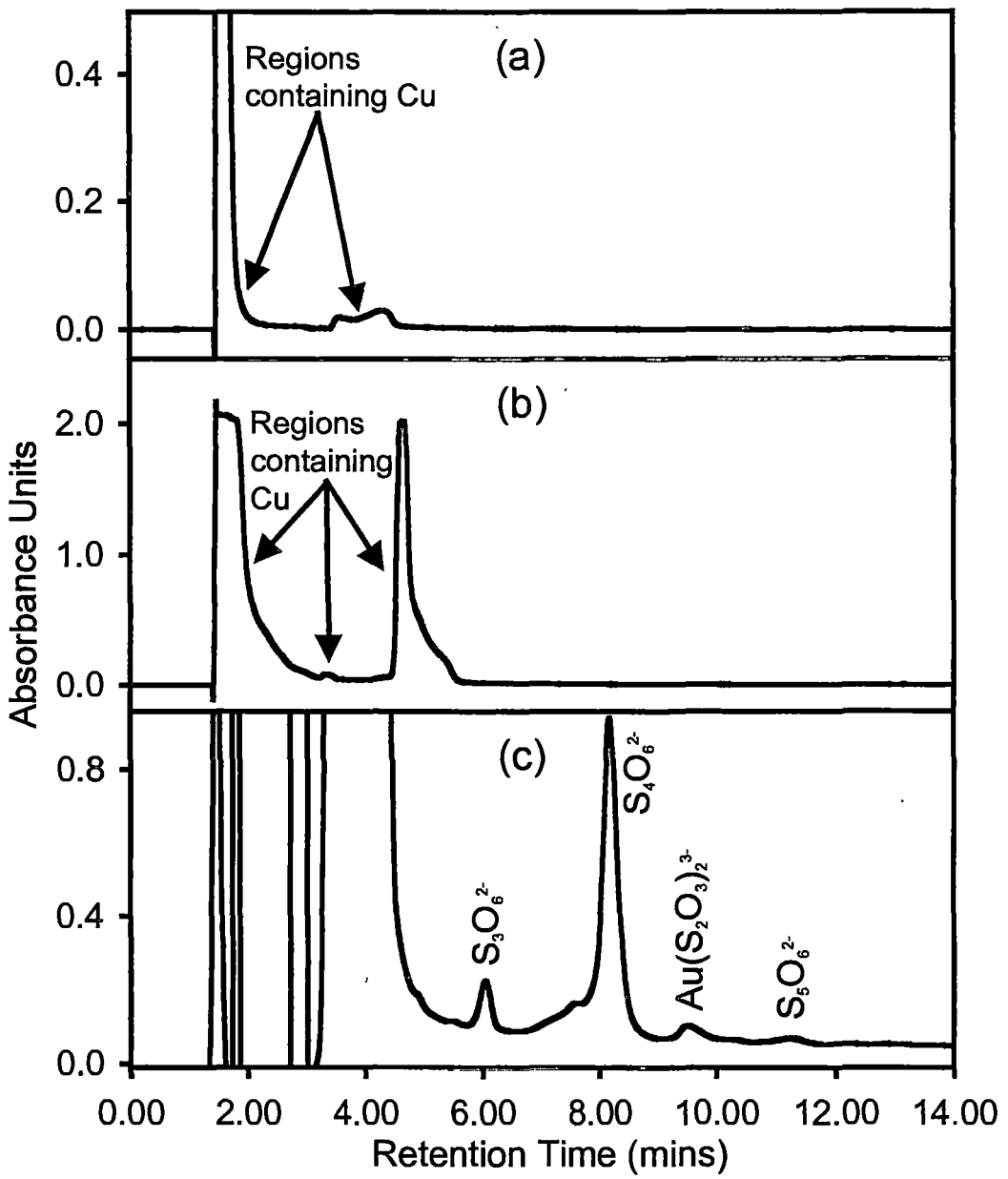

Fig. 4.4 (a) Chromatogram obtained at 510 nm for the artificial leach solution (0.5 M ammonium thiosulfate, 2 M ammonia 0.05 M copper sulfate, 0.508 mM (100 mg/L) gold(I) (as thiosulfate) using the optimised separation conditions, with PAR as post-column reagent. (b) Identical chromatogram of the same solution using a 100 µL injection volume. (c) UV chromatogram of the same leach solution for comparison (10 µL injection volume).

remains unidentified. Another possibility that was not investigated is that the shoulder actually corresponds to further tetrathionate, generated on-column through reaction of copper(II) and thiosulfate prior to their resolution.

4.3.3 Linearity and Detection Limits

The detection limits for the polythionates using the optimised method were determined using a 10 µL injection volume, with the limit taken as the concentration of analyte registering a peak two times the peak to peak baseline noise. Linearity was tested from the detection limit to 10.4 mM (2000 mg/L) for trithionate, 8.92 mM (2000 mg/L) for tetrathionate and 9.75 mM (2500 mg/L) for pentathionate. Least squares lines of best fit for the data yielded R^2 values of >0.999, for both conductivity and UV detection. Closer investigation of the calibration plots indicated that the data points deviated significantly from the line for the low concentration polythionate solutions. It was therefore more accurate in most cases to define two lines of best fit, one for low and another for high concentrations. Detection limit and linearity data (without the presence of thiosulfate in the eluent) are summarised in Table 4.2. Before the linearity and detection data were determined, it was deemed necessary to ensure that the polythionates did not interact with one another on the column, which would have affected quantification. This was investigated by preparing a solution containing 1.06 mM (203 mg/L) trithionate, 0.896 mM (201 mg/L) tetrathionate and 1.16 mM (298 mg/L) pentathionate and comparing the peak area obtained against standards of the same concentration injected individually. No significant differences were observed, thus it was concluded that there was no significant interaction between these ions.

Table 4.2 Polythionate detection limit and linear range data for the optimised method by both conductivity and UV detection.

Analyte	Detection Limit, μM (mg/L)		Linear range, mM (R^2 values)	
	Conductivity	UV	Conductivity	UV
Trithionate	5 (1)	68 (13)	0.026-0.52 (0.9998) 0.26-10.4 (0.9999)	0.26-10.4 (0.9999)
Tetrathionate	13 (3)	4 (0.8)	0.045-0.89 (0.9998) 0.45-8.9(0.9994)	0.022-5.4 (0.9999) 0.22-8.9 (0.9999)
Pentathionate	23 (6)	4 (1)	0.098-2.0 (0.9999) 2.0-9.75 (0.9995)	0.023-2.0 (0.9999) 2.0-9.75 (0.9992)

Reproducibility data was calculated from triplicate 10 µL injections of the linearity standards. Using conductivity detection polythionate concentrations of ≥ 0.10 (20) ($S_3O_6^{2-}$), ≥ 0.45 (100) ($S_4O_6^{2-}$) and ≥ 0.49 (125) ($S_5O_6^{2-}$) mM (mg/L) all yielded peak area reproducibility values of < 2% RSD. The equivalent concentrations for UV detection were 4.2 (800), 0.22 (50) and 0.39 (100) mM (mg/L). The high concentration for trithionate when using UV detection reflects the comparatively high detection limit for this ion.

If required, the detection limits could be reduced by using a larger injection volume. This may be necessary for the determination of pentathionate, which is present in much lower concentrations than the tri- and tetrathionate in the leach solutions. Equally, if polythionate concentrations increased above the tested range, a smaller injection volume or dilution may be required.

In view of the complex nature of the leach solution, it would be normal to consider matrix matching between the standards and samples. This is inappropriate here since the matrix contains the species under examination and for reasons discussed in the introduction, the concentrations present change with time, prohibiting any use of a standard addition method. Matrix matching the thiosulfate content of the leach was also not possible due to Eqns. 1.7-1.9 (Section 1.5.3) whereby the thiosulfate will catalyse decomposition of the polythionates. For these reasons, all standards were prepared in Milli-Q water only.

4.3.4 Analysis of an Actual Leach Solution

Fig. 4.5 shows UV chromatograms from thiosulfate leach liquors of (a) oxide and (b) sulfide gold ore concentrates with the sample in each case taken five hours after leaching was commenced. Fig. 4.6 demonstrates the variation of polythionate concentrations in the sulfide ore leach over a five-hour period, determined using the optimised methodology. Polythionate concentrations were determined by comparison to three point calibration curves. The chromatograms indicate that the method was able to handle the leach conditions and both ore types reasonably well, although the shoulder peak previously noticed in the artificial leach solutions was still present, in addition to another unknown peak at 5.25 min. This second peak does not interfere with the analysis and was not identified. Using the PCR system described previously, no peak corresponding to the retention time of this unknown peak was observed, indicating that it was not a copper complex or that of any other metal that reacts with PAR.

Fig. 4.6 shows that the maximum values for tetra- and pentathionate occurred at the start of the leach, and then dropped slowly with time, possibly moving towards an equilibrium or steady state concentration. The comparatively high pentathionate concentration at the start of the leach was probably a result of equilibrium disturbances (see Eqn. 1.14, Section 1.6.2) caused by the rapid generation of tetrathionate. As the rate of tetrathionate formation decreased the formation of pentathionate would have also slowed. It is likely then that eventually alkaline decomposition of pentathionate occurred at a faster rate than the formation reaction, resulting in the observed decline in pentathionate concentration as the leach progressed.

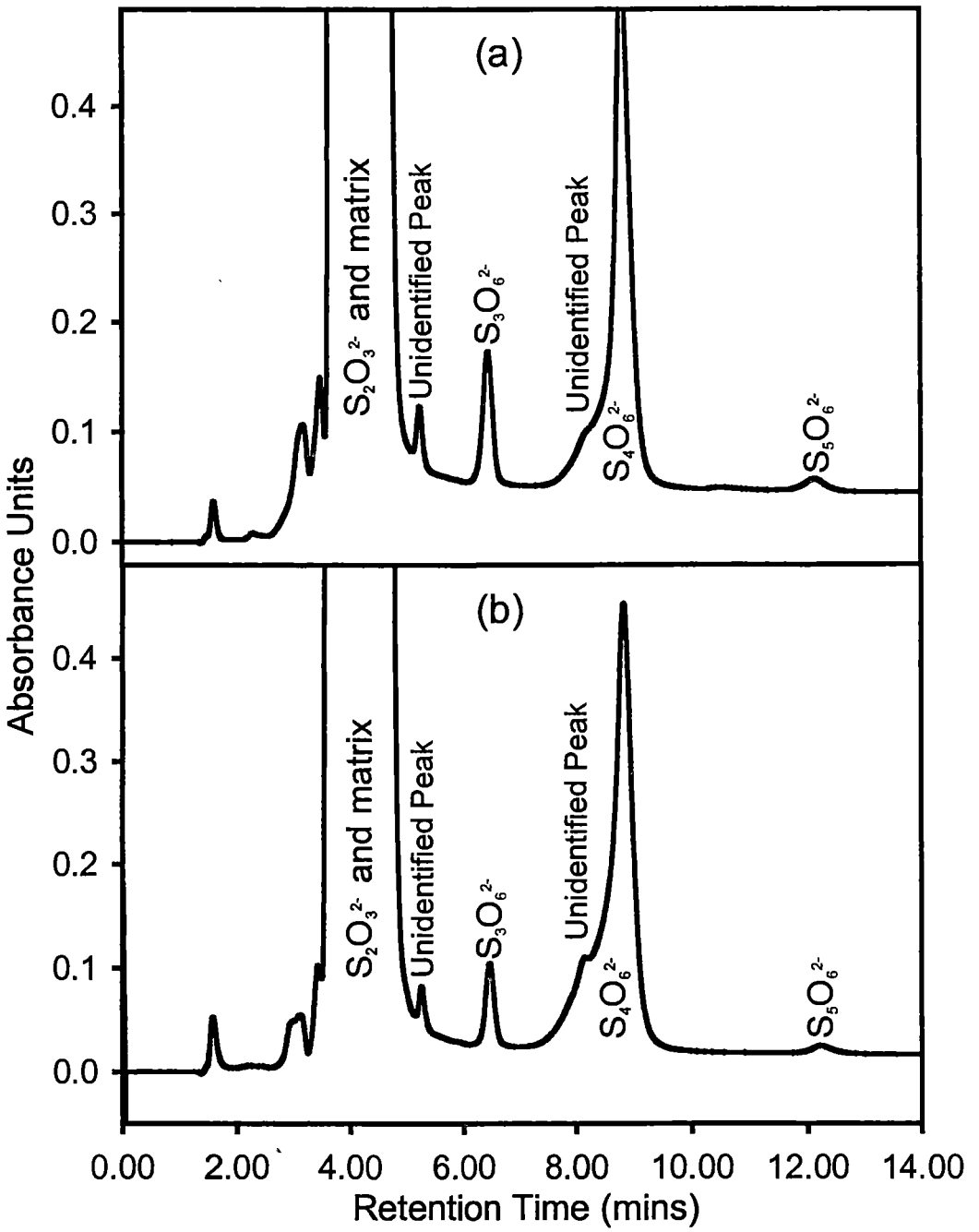

Fig. 4.5 UV chromatograms from gold thiosulfate leach solutions of (a) an oxide and (b) a sulfide ore concentrate, obtained from samples extracted 5 h after leaching was commenced. For leach conditions refer to Chapter 2 Section 2.2.2. Optimised analytical conditions used. The concentrations of polythionates in the oxide ore were 3.5 mM (792 mg/L) for tetrathionate and 0.074 mM (19 mg/L) pentathionate with the trithionate concentration above the tested linear range. The corresponding values for the sulfide ore were 8.9 mM (1716 mg/L) trithionate, 3.7 mM (822 mg/L) tetrathionate and 0.043 mM (11 mg/L) pentathionate.

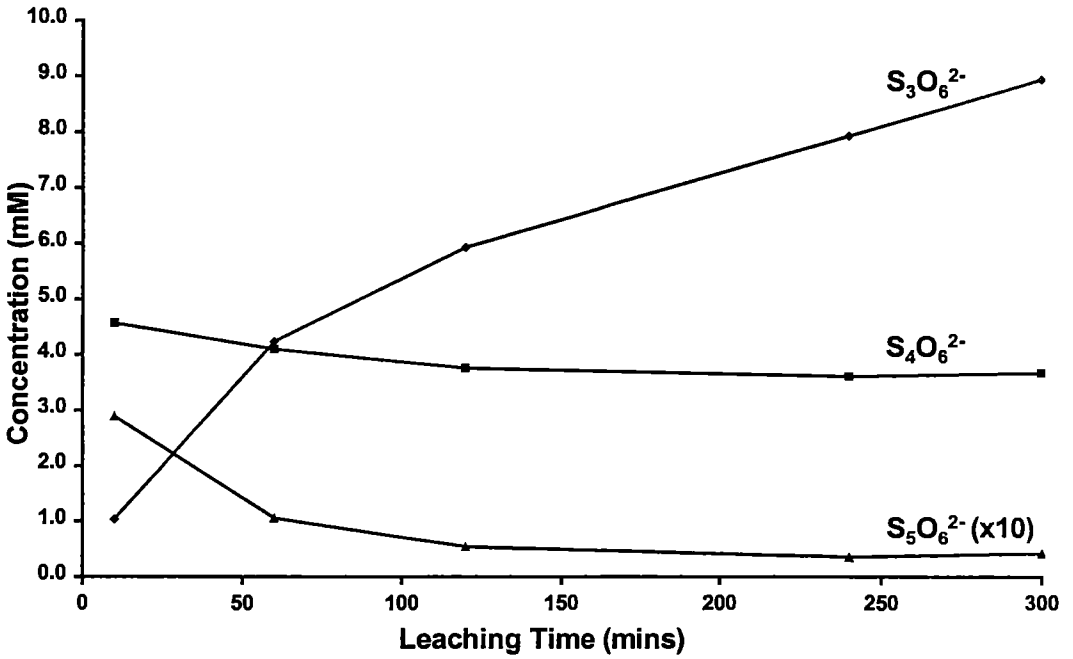

Fig. 4.6 Plot of polythionate concentrations as a function of leach time, taken from the results of a thiosulfate leach of a sulfidic gold ore concentrate. Analytical and leach methodology as per Fig. 4.5.

In contrast to the other polythionates, the trithionate concentration increased throughout the monitored period, initially lower than tetrathionate, increasing to twice the concentration of this ion by the end of the five hours. This was most likely generated through tetrathionate decomposition (Eqns. 1.7.-1.9, Section 1.5.3). The build-up in concentration of this species over the entire leaching period probably related to the comparative stability of trithionate in alkaline solutions.

4.4 Conclusions

A method for the successful determination of polythionates in complex leach liquors with good sensitivity and selectivity has been developed. While the method also demonstrated the first reported chromatographic separation of gold thiosulfate in standard solutions, the results for leach solutions were disappointing and a self-elution effect prohibited successful analysis by this technique.

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Chapter 5

Separation of Thiosulfate, Polythionates and the Gold Thiosulfate Complex in Gold Thiosulfate Leach Solutions by Capillary Electrophoresis

5.1 Introduction

The preceding investigations into the ion-interaction chromatography of the gold thiosulfate complex demonstrated many problems, which prevented its determination by this technique in leach solutions. Two factors that were hypothesised to cause, or at least contribute to this were a self-elution effect and decomposition induced by the stationary phase packing of the column. Both relate to the chromatographic methodology itself, and therefore a significant improvement in gold peak stability should be observed if the separation could be facilitated by means other than through interaction with a surface; that is, not requiring a stationary phase. CE is such a technique (described in Section 1.6.4.1), since open tubular capillaries are used, and the mode of separation is completely different to IC. The negative charges on the only surface present in the capillary, that of the fused silica wall, should actually repel the gold complex. CE may also offer some other advantages over the IC method demonstrated in Chapter 4, particularly in terms of the much faster and efficient separations achievable, which would be advantageous in a process-monitoring situation.

This chapter therefore describes investigations into the capability of this technique in the separation and determination of thiosulfate, polythionates and the gold thiosulfate complex in simple mixtures and gold thiosulfate leach solutions.

5.2 Experimental

5.2.1 Instrumentation

All CE experiments were performed on an Agilent Technologies ^{3D}CE (Waldbronn, Germany), equipped with a photodiode array detector. Fused silica capillaries (Polymicro Technologies, Phoenix, AZ, USA), of effective length 40 cm, total length 48.5 cm and a 75 μm internal diameter, were used throughout. All experiments were performed at a capillary oven temperature of 30°C with an applied voltage of –30kV unless otherwise specified. Injection was made using a pressure of 50 mbar applied for 3 s. Data were collected using Agilent Technologies ^{3D}CE ChemStation software.

For pH adjustments, an Activon (Thornleigh, NSW, Australia) Model 210 pH meter was used.

5.2.2 Procedures

For pH adjustment (where necessary) sulfuric acid was used unless otherwise specified. Sodium hydroxide solutions were prepared from a ~50% w/w stock solution.

At the beginning of each day the capillary was flushed with 1 M sodium hydroxide for 15 min, water for 15 min and electrolyte for 10 min. Between each

run the capillary was flushed with 1 M sodium hydroxide for 1 min, and twice for 1 min with electrolyte (from separate vials).

Details of the methodology used to conduct the leaching experiment has already been provided in Chapter 2, although note samples were diluted as well as filtered prior to analysis.

5.3 Results and Discussion

5.3.1 Preliminary Investigations

As a starting point, the two methods outlined by Padarauskas et al. [1] for the analysis of thiosulfate, tetrathionate, pentathionate and hexathionate were examined for their capability to also simultaneously determine trithionate and the gold thiosulfate complex. Neither method was suitable, with the first electrolyte (5 mM potassium dihydrogen phosphate, 5 mM ammonium sulfate at pH ~5) being unable to provide baseline resolution of gold thiosulfate from trithionate peaks, whilst the second electrolyte (5 mM tetrabutylammonium acetate, 5 mM ammonium sulfate pH 5.0) resulted in co-migration of trithionate and the gold thiosulfate complex. Varying the oven temperature in the range 25-40°C and increasing the TBA^+ concentration in the electrolyte also gave unsatisfactory separations.

Several restrictions had to be considered in selecting an alternate electrolyte system. The electrolyte pH needed to be greater than 5 since thiosulfate is known to be unstable at lower pH values [1,2], and the electrolyte should also be buffered in order to minimise migration time irreproducibility [3]. Padarauskas [1] noted

problems with the use of tetradecyltrimethyl ammonium hydroxide as an electro-osmotic flow (EOF) modifier, causing broad, poorly shaped peaks for the polythionates, while the use of 1,6-bis(trimethylammonium)hexane hydroxide, was found to cause similar problems for hexathionate only. Although hexathionate was not under consideration as an analyte in the present study, it was decided to keep the electrolyte free of EOF modifier. This prevented the use of alkaline electrolytes since this would result in high EOF values and unacceptably long migration times. Other requirements were that the electrolyte did not absorb significantly at the UV detection wavelength, and the mobility of the electrolyte co-anion needed to be close to those of the analytes to prevent poor peak shapes. Based on these criteria bis-tris sulfate (pK_a of 6.46 [4]) at pH 6.0 was chosen as the electrolyte.

5.3.2 Optimisation of Electrolyte Composition

Fig. 5.1 shows the effect of the concentration of bis-tris in the electrolyte on the mobility of the analytes (relative to thiosulfate). With increasing electrolyte concentration the relative mobilities of the polythionates increased marginally, while that for the gold thiosulfate complex decreased substantially. The behaviour of the gold complex can be attributed to ion-association with bis-tris [5], due to the triple negative charge of the complex. An effect not apparent in Fig. 5.1 is that the effective mobilities of all anions increased with increasing bis-tris concentration due to a reduction in the EOF as a result of increased ionic strength of the electrolyte. The optimal electrolyte composition was 25 mM bis-tris adjusted to pH 6.0 with sulfuric acid and Fig. 5.2 shows the separation of the analytes under these conditions, with detection at 195 nm.

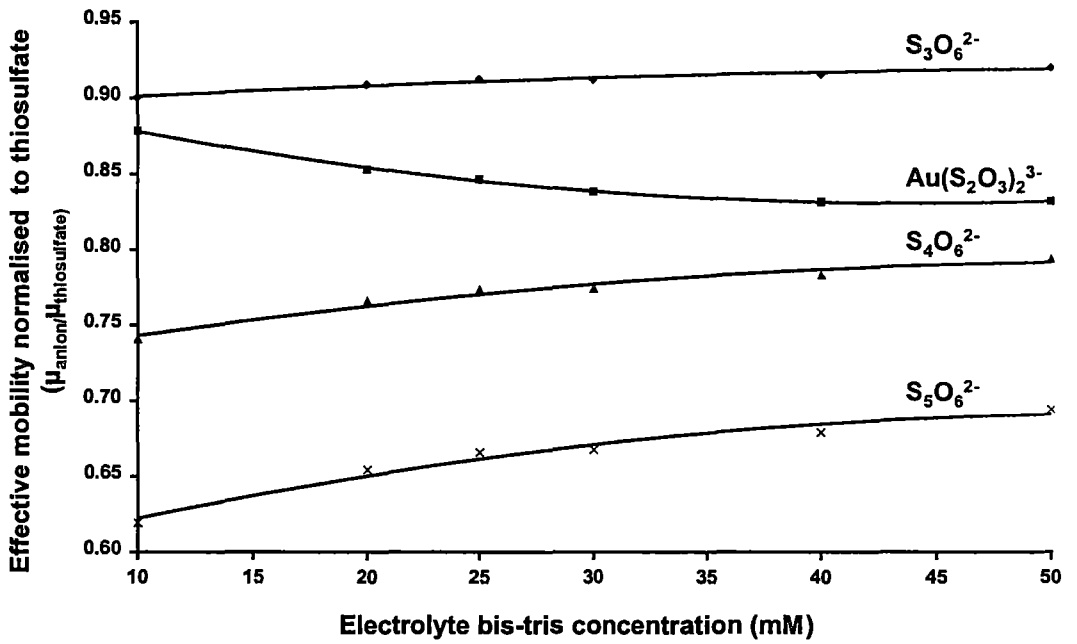

Fig. 5.1 Mobilities of gold thiosulfate and the polythionates relative to thiosulfate, as a function of electrolyte bis-tris concentration. All electrolytes were adjusted to pH 6.0 with sulfuric acid. For other conditions see Section 5.2.

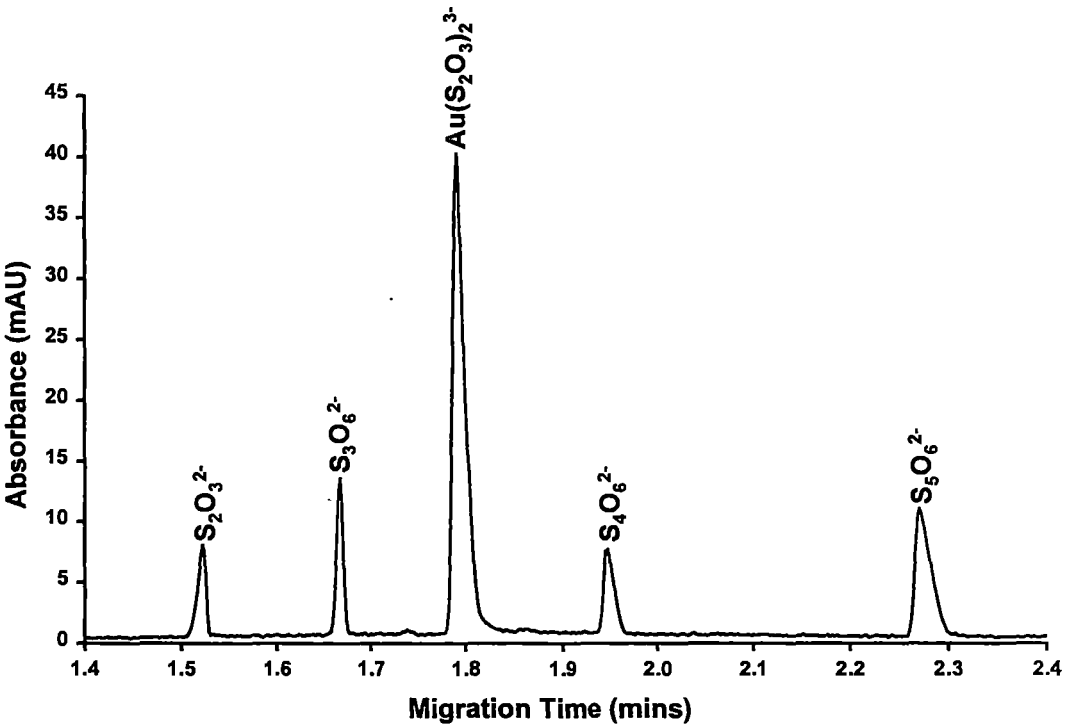

Fig. 5.2 Separation of 0.1 mM thiosulfate and 0.08 mM each of trithionate, tetrathionate, pentathionate and the gold thiosulfate complex using the optimum electrolyte conditions. Electrolyte contained 25 mM bis-tris adjusted to pH 6.0 with H_2SO_4, and a detection wavelength of 195 nm was used. For other conditions see Section 5.2.

During the preliminary experiments and optimisation it was found that the hydroxide concentration of the flush solution markedly influenced the effective mobilities of the analytes, with concentrations weaker than that specified in the experimental section resulting in significantly longer migration times. This was attributed to decreased EOF. Under the optimal conditions all the species of interest could be separated in less than 3 min, with a total analysis time (including capillary pre-flushing) of 8 min.

5.3.3 Behaviour of the Gold Thiosulfate Complex

As discussed in Chapters 3 and 4, the gold thiosulfate complex was found to be indeterminable in leach matrices by IC, mainly through what was attributed to a self-elution effect. One of the aims of this work was to investigate whether CE, would permit simultaneous determination of this complex and the polythionates. Unfortunately, the behaviour of the gold thiosulfate in the CE system was not straightforward.

When standard solutions of the gold complex exceeding ~0.05 mM (~10 mg/L Au) were injected, a section of raised baseline immediately following the gold thiosulfate peak was usually observed (Fig. 5.3(a)). In the presence of relatively high concentrations of some sulfur-oxygen matrix ions, particularly thiosulfate, peak splitting occurred until eventually three peaks could be discerned. Typical shapes of the gold peak in the presence of 1 mM thiosulfate, trithionate and tetrathionate and 5 mM thiosulfate are illustrated in Fig. 5.3(b) and (c) respectively. Low concentrations of thiosulfate and/or polythionates in samples did not affect the gold peak significantly, as evidenced by the electropherogram in Fig. 5.2. Peak II exhibited an UV spectrum similar to that for the main gold

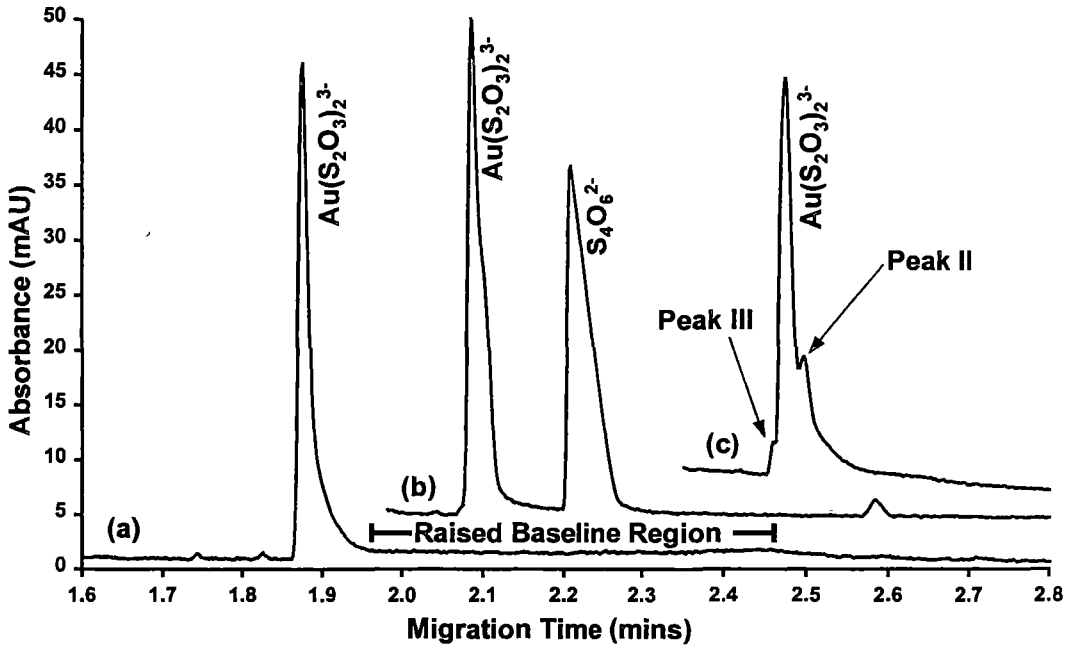

Fig. 5.3 Effect of sample matrix on the peak shape for the gold thiosulfate complex. Electropherograms of 0.13 mM gold thiosulfate in the presence of **(a)** no other matrix ions, **(b)** 1 mM thiosulfate 1 mM trithionate and 1 mM tetrathionate (shifted forward 0.3 mins) and **(c)** 5 mM thiosulfate (shifted forward 0.6 mins). Separation conditions as per Fig. 5.2.

thiosulfate peak, while that of peak III was similar to those of thiosulfate and tetrathionate, however positive identification was not possible. A related problem was that the behaviour of the gold peak was related to the injection history of the capillary, with peak area being increased after injection of high thiosulfate matrices.

The appearance of multiple peaks could be due to an equilibrium between the mono- ($Au(S_2O_3)^-$) and bis- thiosulfate ($Au(S_2O_3)_2^{3-}$) complexes. It would be expected that mobility of the mono-thiosulfate complex would be considerably lower than that of the bis-complex. This equilibrium would also be sensitive to thiosulfate, the presence of which in the system would result in the equilibrium shifting to favour formation of the bis-complex. Whilst no thermodynamic data for the gold mono-thiosulfate complex could be located, there are literature references to the labile nature of the gold thiosulfate complex [6].

Due to the inconsistencies observed for peak area and shape of the gold thiosulfate complex, particularly for samples containing high thiosulfate matrices, it was not possible to quantify this species by CE under the conditions used in this work.

5.3.4 Linearity and Detection Limits

The detection limits and linearity ranges for the optimised method are given in Table 5.1. Linearity was tested from the detection limit to 8 mM for thiosulfate, and to 2 mM for trithionate, tetrathionate and pentathionate. A detection limit for the gold thiosulfate complex was also calculated. Because of the different UV absorbance maxima of the analytes the results for thiosulfate, tetrathionate and

Table 5.1 Thiosulfate, gold thiosulfate and polythionate detection limit and linear range data using the optimised CE method with UV detection at the specified wavelengths.

Analyte	Detection Wavelength (nm)	Detection Limit (μM) (S/N = 3)	Linear Range (μM) (R^2 value)
Thiosulfate ($S_2O_3^{2-}$)	214	2	40-8000 (0.9989)
Gold Thiosulfate ($Au(S_2O_3)_2^{3-}$)	195	0.5	-
Trithionate ($S_3O_6^{2-}$)	195	1	10-2000 (0.9998)
Tetrathionate ($S_4O_6^{2-}$)	214	1	10-2000 (0.9998)
Pentathionate ($S_5O_6^{2-}$)	214	0.5	5-2000 (0.9998)

pentathionate were determined at 214 nm, while for trithionate and gold thiosulfate 195 nm was used. The limits were determined as the concentration of each species giving a signal to noise ratio of 3:1. Thiosulfate was prepared as separate standards because of the risk of interactions with the polythionates, as shown previously in Eqns 1.7 to 1.9 (Section 1.5.3).

Reproducibility of the method was determined using a solution of 0.1 mM thiosulfate and 0.08 mM each of trithionate, tetrathionate and pentathionate. Migration time reproducibility was < 1% RSD and reproducibilities of normalised peak areas were < 3% RSD for all four ions based on 12 replicate injections.

5.3.5 Analysis of Leach Solutions

A wide range of leach conditions can be found in the literature, with a recent review reporting extremes of 0.1-2 M for thiosulfate, 0.1-6 M ammonia and 0.001 – 0.1 M copper(II) [7]. Based on this source and our own experience, we estimate that 70% of reported leaching regimes use conditions containing $\leq$ 0.5 M thiosulfate, $\leq$ 2 M ammonia and $\leq$ 0.05 M copper(II). For the purposes of this study a leaching regime consisting of 0.5 M $(NH_4)_2S_2O_3$, 2 M NH_3 and 0.05 M $CuSO_4$ was chosen to evaluate the developed CE method.

The copper in the leach solutions can exist in a variety of forms including amine and thiosulfate complexes. The thiosulfate complexes most likely to occur are the bis- ($Cu(S_2O_3)_2^{3-}$) and tris- ($Cu(S_2O_3)_3^{5-}$) forms which could potentially migrate in a similar region to the anions of interest. However, solutions containing 16 mM thiosulfate and 1 mM copper(II) (dissolved as sulfate) showed no copper peak, perhaps due to precipitation as an insoluble mono-thiosulfate cuprous complex or

the formation of a positively charged complex with bis-tris. The presence of ammonia in the leach solution could be further expected to reduce the amount of negatively charged copper-thiosulfate complexes. For these reasons, no interference effects from copper or its complexes were observed.

A well known problem with CE is its difficulty in handling samples of high ionic strength [8]. In order to obtain acceptable peak profiles, samples should have an ionic strength less than one third that of the electrolyte solution [9]. This necessitated that the leach solution be diluted prior to analysis and for the leaching regime chosen, a dilution factor of 1 in 100 was appropriate. This dilution step resulted in higher effective detection limits for the sample and also increased the sample handling time prior to analysis which provides a longer time during which changes in the sample speciation could occur. It was therefore imperative that the samples were analysed as soon as possible after sampling.

Fig. 5.4 shows the UV electropherogram obtained from the injection of a sample obtained from a leach of a sulfidic gold ore concentrate. Fig. 5.5 shows the results of monitoring the leach over a period of nearly 6.5 h. The concentrations were evaluated against a three-point calibration curve for each of the analyte ions. Pentathionate was present in high enough concentrations to be observed initially in the leach solution, but its concentration diminished over time to below the effective quantitation limit of 0.5 mM. Overall, the trends apparent for all the polythionates in Fig. 5.5 are consistent with those from the corresponding study in Chapter 4 that used IC (Fig. 4.6).

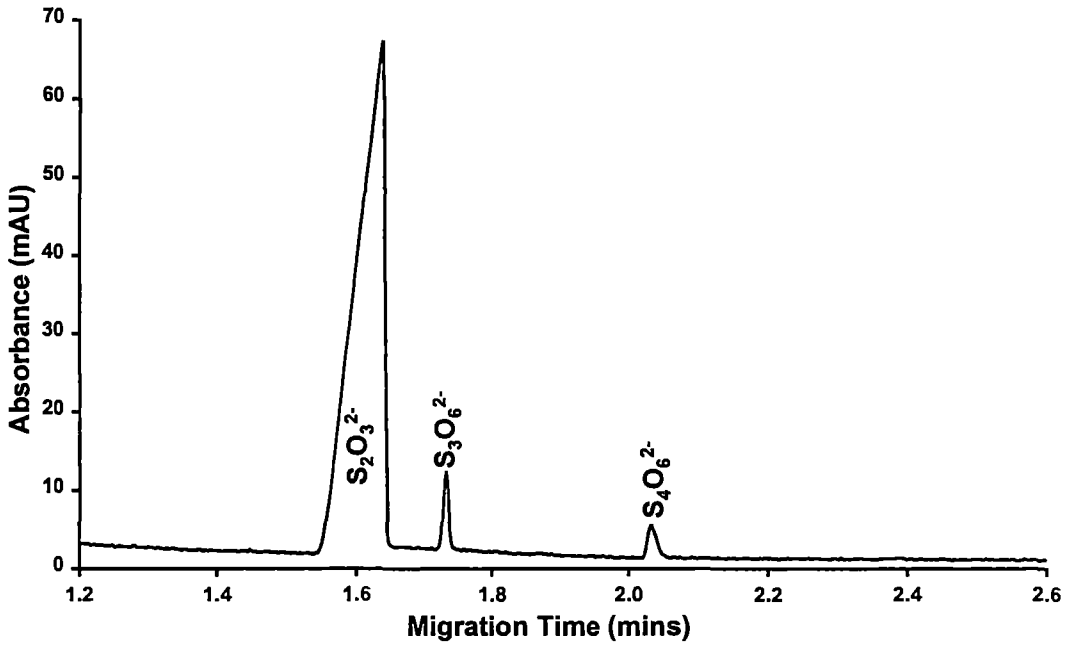

Fig. 5.4 Electropherogram of a 1:100 diluted thiosulfate leach solution of a sulfidic gold ore 1 h after leaching was commenced. Conditions as per Fig. 5.2.

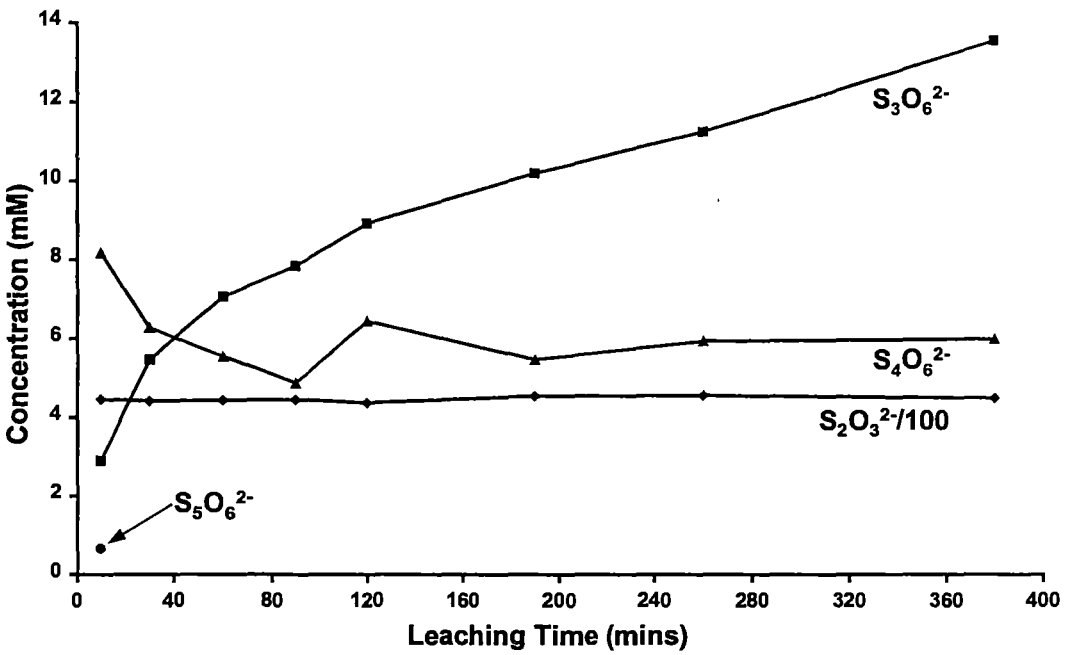

Fig. 5.5 Plot of thiosulfate and polythionate concentrations as a function of time, taken from the thiosulfate leach of a sulfidic gold ore concentrate. Analytical methodology as per Fig. 5.2, except detection wavelength of 195 nm was used only for trithionate, with the remainder detected at 214 nm. For leach conditions refer to Chapter 2, Section 2.2.2.

5.4 Conclusions

The utility of CE for the rapid determination of thiosulfate and polythionates in gold thiosulfate leach liquors has been demonstrated. While the first electrophoretic separation of the gold thiosulfate complex has also been shown, inconsistencies in the peak area and shape caused primarily through the presence of significant quantities of sulfur-oxygen anions in the sample matrix, prevented quantification of the gold complex.

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Chapter 6

Isotachophoretic and Mixed-Mode Electrophoretic Separations of Sulfur-Oxygen Anions in Gold Thiosulfate Leach Solutions

6.1 Introduction

Concern over the dilution factor required in order to facilitate analysis of the gold thiosulfate leach solutions by CE prompted an investigation into the use of ITP, and mixed-mode ITP/CE methodologies. One advantage of ITP over other separation techniques such as IC and CE is its greater capability to handle high ionic strength matrices, minimising the need for dilution and potentially making it a favourable alternative for the analysis of the gold thiosulfate leach matrix. The technique may also enable the simultaneous analysis of four key sulfur anions, namely, thiosulfate, sulfate, trithionate and tetrathionate in leach solutions, which has not been previously achieved.

Therefore, this chapter outlines a preliminary investigation into the utility of ITP for the separation and analysis of sulfur anions in gold thiosulfate leach liquors. The developed method is applied to the determination of thiosulfate and sulfate in these solutions. Also examined is the use of a mixed-mode ITP/CE separation to determine whether this approach has any advantages over the developed CE and ITP methodology.

6.2 Experimental

6.2.1 Instrumentation

All capillary electrophoretic experiments were performed on an Agilent Technologies ^{3D}CE (Waldbronn, Germany), equipped with a photodiode array (PDA) detector. Separations were conducted in coupled fused silica capillaries (Polymicro Technologies, Phoenix, AZ, USA), consisting of a 20 cm 250 μm I.D. segment joined to a 28.5 cm 75 μm I.D. segment by means of a Teflon sleeve (~1 cm). The effective length of the capillary was 40 cm with the detection window in the 75 μm segment. All separations were performed at a capillary oven temperature of 30°C using a variety of different driving currents, some involving a simple step gradient. Injection was performed using a pressure of 50 mbar applied for 3 s. Data collection was performed using Agilent Technologies ^{3D}CE ChemStation software, with a data acquisition rate of 10 Hz unless otherwise specified.

The mixed-mode ITP/CE work was conducted on similar instrumentation with similar conditions to the pure ITP method, except using only 75 μm I.D. capillaries of 40 cm effective and 48.5 cm total length unless otherwise specified.

For pH adjustments, an Activon (Thornleigh, NSW, Australia) Model 210 pH meter was used.

6.2.2 Procedures

The bis-tris buffer solutions were adjusted to the required pH using the acid of the anion required for the electrolyte. Sodium hydroxide solutions were prepared from a ~50% *w/w* stock solution.

Capillary flushing procedures were the same as described in Chapter 5. For calibration purposes injections of each standard were made at least in duplicate. To minimise carry-over problems the terminating electrolyte solution was replaced after each analysis, and the outside of the capillary inlet was cleaned by cycling the instrument through 3 electrolyte vials containing milli-Q water between each analysis.

The synthetic leach solution used to assess the utility of the technique for this matrix was prepared in a beaker that was thereafter covered with a watchglass. The solution was left at room temperature with slow mechanical stirring.

The locations of the zone boundaries were determined from the derivative plot of each phcrogram.

6.3 Results and Discussion

6.3.1 Preliminary Investigations and Development of the ITP System

Thiosulfate has the highest mobility of the ions under consideration in this work, and is actually of higher mobility than most anions used commonly as the leading ion in ITP systems. It is therefore difficult to find a suitable leading ion without adding a modifier to the buffer to selectively reduce the effective mobility of

thiosulfate. In the existing literature this has been achieved in one of two ways, through the preparation of the leading electrolyte in a 1:1 mixture of acetone and water [1], or the addition of calcium(II) as an ion-association reagent [2,3]. Either method enabled chloride to be used as the leading electrolyte anion. Because of concern that components of the leach matrix may precipitate as a result of either the high proportion of organic solvent in the former system or the possibility of calcium sulfate precipitation in the latter, neither systems could be utilised in this study. Earlier research undertaken in our laboratory using CE [4] have determined that electrolytes containing bis-tris (pK_a = 6.46 [5]) as a cationic buffering reagent decreased the effective mobility of thiosulfate and the polythionates relative to the monovalent ions bromide, iodide and nitrate, presumably through an ionic-strength and/or an ion-association mechanism. It was therefore expected that the use of a sufficient concentration of this ion in the leading electrolyte could potentially provide the basis for an electrolyte system where thiosulfate had an effective mobility lower than that of chloride. Initially, a leading electrolyte containing 60 mM bis-tris was used, (adjusted to pH 6.4 with hydrochloric acid), since this had previously been found to reduce the effective mobility of thiosulfate in a CE system to below that of bromide [4]. To suppress the electro-osmotic flow (EOF) in the capillary, the EOF suppressant hydroxypropylmethylcellulose (HPMC) was used at a concentration of 0.05% *w/v* in combination with the comparatively high ionic-strength of the leading electrolyte. The terminating electrolyte used was initially 10 mM sodium formate. The initial current settings were –90 μA changing to –20 μA at 11 min. The non-UV-absorbing analyte sulfate was identified by the presence of a low absorbance band between two zones of UV-absorbing analytes. The remaining

zone identifications were made via the use of the PDA spectra. Testing was performed using a solution theoretically containing 50 mM thiosulfate, 20 mM sulfate and 5 mM trithionate. The term "theoretically" is used since tetrathionate is formed in the sample through mixing of trithionate and thiosulfate.

Using the initial system, the sulfur anions were found to migrate in the order thiosulfate < trithionate < sulfate < tetrathionate, but the boundary between trithionate and sulfate was poorly defined due to incomplete zone separation. There was also a poorly defined boundary between the zones for the chloride leading electrolyte and thiosulfate. Further testing indicated that the presence of significant chloride concentrations in the sample matrix influenced the zone length of the thiosulfate band, which impeded quantification.

In order to solve these problems, a further ion-pair reagent, tetrabutylammonium chloride (TBA^+Cl^-), was also added to the leading electrolyte. The concentration of TBA^+ was found to influence the separation of trithionate and sulfate, actually reversing the migration order of these species. A TBA^+ concentration of 10 mM added to the 60 mM bis-tris containing leading electrolyte, was found to give a satisfactory separation of sulfate, trithionate and tetrathionate ions, but did not however improve the definition of the chloride/thiosulfate boundary. A bis-tris concentration of 120 mM (adjusted to pH 6.4 with hydrochloric acid, also containing 10 mM TBA^+Cl^- and 0.05% *w/v* HPMC) was observed to improve the boundary between chloride and thiosulfate markedly, but also resulted in incomplete separation of the sulfate and trithionate zones. Increasing the TBA^+ concentration of the leading electrolyte to 20 mM rectified this problem with only

a slight decrease in the sharpness of the chloride/thiosulfate boundary. Finally, the hold up time was found to be more reproducible when a buffered terminating electrolyte was used and for this reason a terminating electrolyte containing 20 mM bis-tris adjusted to pH 6.4 with formic acid was adopted. The optimised ITP system employed was a leading electrolyte comprising120 mM bis-tris, 20 mM TBACl, 0.05% HPMC adjusted to pH 6.4 with hydrochloric acid, a terminating electrolyte comprising 20 mM bis-tris, adjusted to pH 6.4 with formic acid, and an operating current of -110 μA. All other conditions were as specified in Section 6.2.1. With this electrolyte system, the analysis time including capillary pre-flushing procedures was less than 30 min, which is unfortunately significantly longer than the IC and CE methods described previously.

Due to time constraints it was not possible to thoroughly investigate the method for its capability to simultaneously determine all four of the sulfur anions discussed in the introduction to this chapter, namely, thiosulfate, sulfate, trithionate and tetrathionate. As a result it was decided at this point to focus on the determination of thiosulfate and sulfate, and leave the polythionates for future work.

6.3.2 Linearity, Detection Limits and Reproducibility

Problems were encountered with the reproducibility of the injection volume and it was therefore necessary to use an internal standard. Thiocyanate, used at a concentration of 40 mM, was chosen for this role since it has an effective mobility between trithionate and tetrathionate in this system. To confirm that there was no interference between thiocyanate and either of the polythionates a solution containing ~20 mM each of tri- and tetrathionate in addition to 40 mM

thiocyanate was injected. There were no mixed zones evident between these species in this solution and the boundaries were sharp. It was therefore concluded that no interferences existed.

Detection limits for the method were 2.1 mM for thiosulfate and 1.3 mM for sulfate, determined as three times the standard deviation observed for triplicate injections of a standard mixture containing 4 mM thiosulfate, 1.4 mM sulfate and the internal standard. Calibration linearity using normalised peak areas was satisfactory in the range 4-200 mM for thiosulfate (R^2 = 0.9999) and 1.4-68 mM for sulfate (R^2 = 0.9989). It should however be noted that the linear range for both thiosulfate and sulfate was determined from a single set of mixed standards, in which the highest concentration solutions contained >200 mM thiosulfate, which could be expected to have affected the observed linear range for sulfate. Linearity was poor when calculated from the absolute zone lengths, with the calibration curves exhibiting behaviour that could not be explained by poor injection volume reproducibility alone. This may relate to the sample ionic strength, and requires further investigation.

Reproducibility of the method was tested using a solution containing 80 mM thiosulfate, 27.2 mM sulfate and 40 mM of thiocyanate and the reproducibility of the normalised zone length was <3% RSD for both species, based on 6 injections.

6.3.3 Analysis of Synthetic Leach Solutions

For the purposes of testing the methodology, a synthetic leachate using the same concentrations of the starting reagents as with the IC and CE work, specifically, 0.5 M $(NH_4)_2S_2O_3$, 2 M NH_3 and 0.05 M $CuSO_4$ was chosen to test the developed

method. Dilution of this sample by a factor of at least 2:5 was required to ensure the concentration of thiosulfate and sulfate were within the linear range. Fig. 6.1 demonstrates an example pherogram from the synthetic leach solution diluted 2:5, obtained after the leach had been in progress for 7.25 hours. The implied concentrations of thiosulfate and sulfate in this sample are 0.415 M and 55 mM respectively, calculated against 3 point calibration curves. Bands for trithionate and tetrathionate in this sample are also visible, offering further evidence that the technique will be useful for simultaneous determination of these anions in leach solutions. The detection limits for these species are expected to be in the low millimolar range, and may therefore not be sufficient for all leach processes and conditions, an effect compounded by any dilution required. For example, small-scale resin-in-pulp leach investigations by Nicol and O'Malley [6] determined that the polythionate concentrations generated in their leachate (20 mg/L or 0.1 mM $S_3O_6^{2-}$, 0.09 mM $S_4O_6^{2-}$) limited the achievable gold loading (~3g/L Au) onto the commercial resin (Amberjet® 4200) used for gold recovery. This indicates a situation where polythionate concentrations need to be monitored at the sub-millimolar level. This potential problem needs to be investigated in future work. The cause of the tailing of the tetrathionate zone should also be investigated, in case it indicates incomplete separation between tetrathionate and the terminating electrolyte.

An investigation was performed into 1:20 dilutions of the synthetic leach solution in order to assess the method for much more dilute solutions. For such injections, the results were complicated by the very short polythionate zones. These were often not long enough for reliable quantification, with the start and end of the

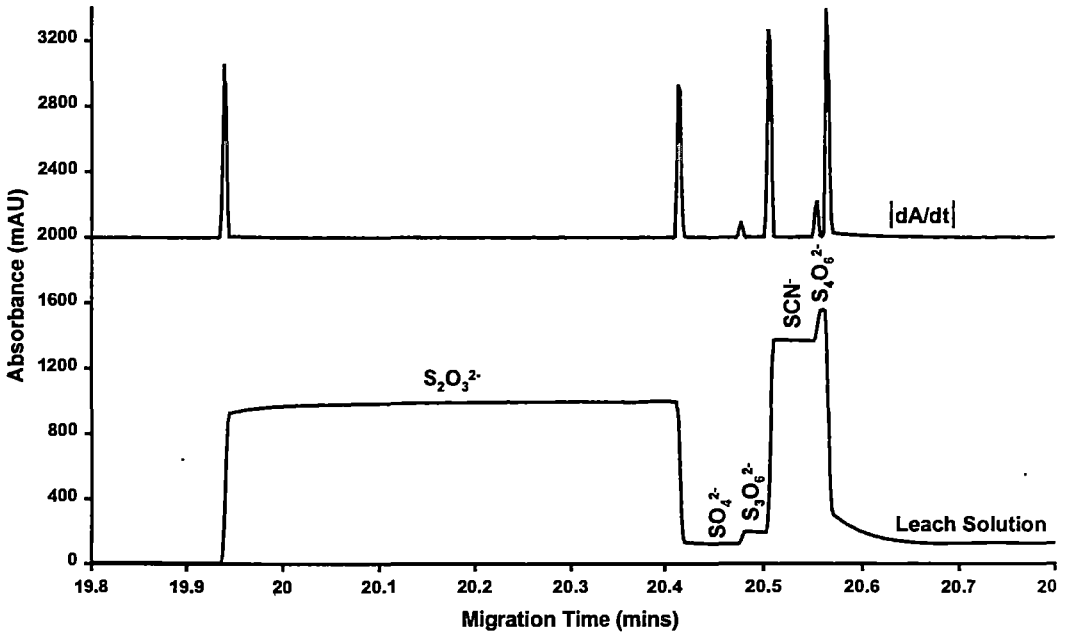

Fig. 6.1. Isotachopherogram of a 2:5 diluted synthetic leach solution sampled 7.25 hours after commencement, with analysis occurring as soon as possible after sampling. Leading electrolyte was 120 mM bis-tris, 20 mM TBACl and 0.05% *w/v* HPMC adjusted to pH 6.4 with HCl, terminating electrolyte was 20 mM bis-tris, adjusted to pH 6.4 with HCOOH. Current was –110 μA and detection was effected at 214 nm. Thiocyanate was added as an internal standard. For remaining conditions see Section 6.2. Note that the y-axis of the figure has no absolute meaning for the derivative plot.

band being too close together to allow resolution between the corresponding derivative peaks. However, these bands were sometimes sizeable enough to introduce an inaccuracy in the measurement of adjacent bands. This problem could be solved for trithionate interference by using both the pherograms recorded at 195 nm and 214 nm. To accurately determine the end of the sulfate band, the 195 nm wavelength was used since the disparity in absorbtivity between sulfate and trithionate is much greater at this wavelength, giving a correspondingly sharper and clearer derivative peak. For similar reasons, the start of the thiocyanate band is calculated using the derivative of the 214 nm pherogram. This approach was not as successful in overcoming the interference from the tetrathionate and the best means of removing this problem was to increase the dilution factor so that the tetrathionate was not detectable.

6.3.4 Investigation into the use of Mixed-Mode ITP/CE Separations

Preliminary investigations into mixed-mode ITP/CE separations were also performed, as it was hoped this would overcome the problems observed with the conventional CE (ionic-strength intolerance) and ITP (analysis time) techniques. Due to a lack of specialised instrumentation it was not possible to use coupled-capillary ITP/CE techniques such as those described previously [7,8]. Single-capillary ITP/CE [9] with a pressure-generated counterflow was also not considered since it would be difficult to implement for a simultaneous determination of all the sulfur-oxygen ions of interest in the leach. Instead, a discontinuous buffer system in a single CE capillary was used, in which only the macrocomponents are separated in the ITP mode (thiosulfate and depending on the concentrations present sulfate and trithionate), with the remaining (lower mobility) anions being separated via a CE mechanism. There does not appear to

be any reference in the literature to the use of such a system, the closest being ITP superimposed on CE, which has been used only as a means of improving detection limits in simple matrices [10].

Initial experiments were conducted using a standard 75 μm capillary with bis-tris/TBA^+ chloride-based leading and sodium perchlorate terminating electrolytes. The aim was to determine thiosulfate, sulfate and trithionate via an ITP mechanism with tetrathionate and possibly pentathionate quantified by CE. Unfortunately, significant baseline problems were observed and it became apparent that simultaneous determination of sulfate could not be achieved since the zone length for this ion was too short. Therefore, the aim shifted to the analysis of thiosulfate and the polythionates only, with thiosulfate separated in the ITP mode, and the polythionates by CE. The optimised leading electrolyte from the earlier ITP work was adopted, while a bis-tris sulfate terminating electrolyte (pH adjusted to 6.0 or 6.4) was used.

Injection of a neat synthetic leach solution (0.5 M $(NH_4)_2S_2O_3$, 2 M NH_3, 0.05 M $CuSO_4$) gave extremely poor results, however a 1:5 diluted portion of this solution produced a pherogram with a clear zone for thiosulfate, followed by separate trithionate and tetrathionate peaks, despite their poor shape. This separation is illustrated in Fig. 6.2(a).

Improvements to the separation for the components migrating in the CE mode were attained by spiking the sample with a low mobility anion such as acetate to act as a transient terminating electrolyte. However this also caused a significant

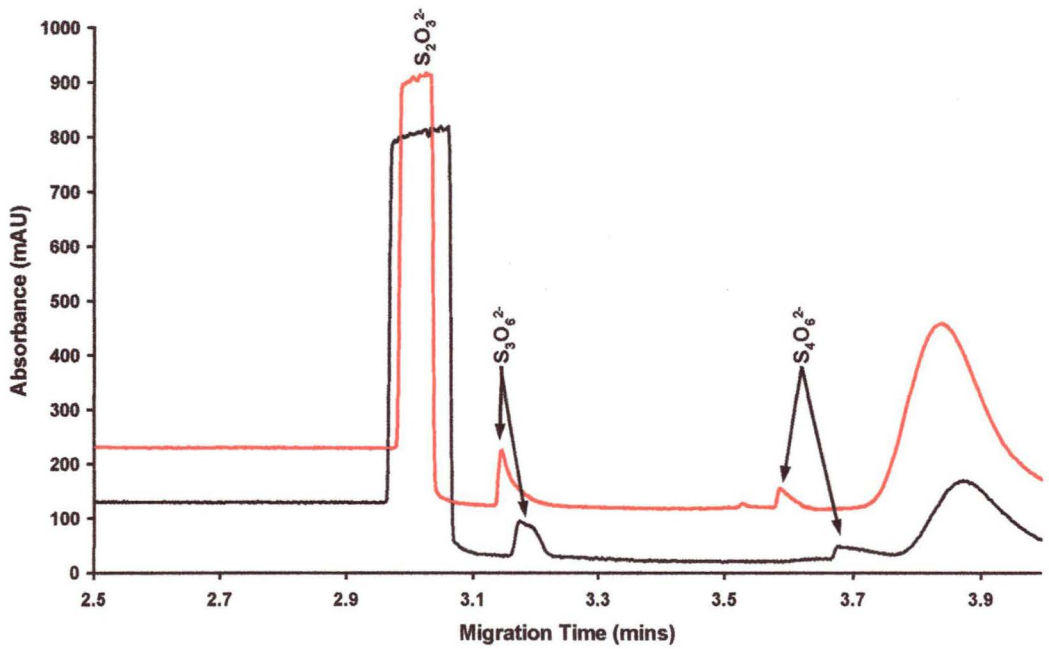

Fig 6.2 (a) 1:5 diluted leach solution initially containing 0.5 M $(NH_4)_2S_2O_3$, 2 M NH_3 0.05 M $CuSO_4$ and 0.4 mM $Na_3Au(S_2O_3)_2$. **(b)** As for (a) except spiked with ~0.6M CH_3COONa. Leading electrolyte 120 mM bis-tris 20 mM TBACl +0.05% *w/v* HPMC adjusted to pH 6.4 with HCl, terminating electrolyte 25 mM bis-tris + 0.05 *w/v* HPMC adjusted to pH 6.4 with H_2SO_4. Driving current –125 µA. For other conditions see Section 6.2. Unknown peak is suspected to be an EOF disturbance coming from the detection side of the capillary.

reduction in the observed peak areas, including those for the thiosulfate zone. The difference in the separations is demonstrated in Fig. 6.2(b). There were also significant peak area reproducibility problems observed throughout this work, particularly for solutions spiked with the transient terminating electrolyte. Investigations employing a simpler matrix containing 0.3 M NaCl and approximately 5 mM each of $K_2S_3O_6$ and $K_2S_4O_6$ were unable to isolate the cause of this problem, although it is almost certainly related to the high ionic strength of the matrices under investigation. It is likely that further dilution of the samples and the use of lower transient terminating electrolyte concentrations is required. As a result of these problems this work was not considered further.

6.4 Conclusions

The utility of isotachophoresis for the determination of thiosulfate and sulfate has been demonstrated in a synthetic leach sample with minimal dilution. Further optimisation of the methodology is required, in order to obtain lower detection limits and allow application of the method to a wider variety of leach regimes. The capabilities of the method for the simultaneous determination of tri- and tetrathionate also need to be assessed. Ways of decreasing the analysis time and improving the reproducibility of the method to remove the need for an internal standard also require investigation.

The concept of single-capillary ITP/CE, without counter-flow, has also been demonstrated for these leach samples. Further work is needed to establish the upper tolerable limit of sample ionic strength (with and without spiking with a transient terminating electrolyte), and also means of improving the reproducibility of the technique.

6.5 References

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Chapter 7

General Conclusions

The following conclusions can be drawn from this study into the chromatographic and electromigrative determination of sulfur-oxygen anions in gold thiosulfate leach solutions.

The chromatographic behaviour of the gold thiosulfate complex in ion-interaction systems was problematic. Matrix-free solutions demonstrated partial dissociation and/or decomposition of the gold complex on-column. This effect could be minimised, but not completely solved, through the addition of thiosulfate to the chromatographic eluent. There was evidence that some of the gold present in such standards precipitated on-column, even in the presence of eluent thiosulfate, although the mechanism or mechanisms involved have not been determined. However, the decomposition of the gold in such standards was reproducible, such that the generation of linear calibration curves for the gold was possible provided that the eluent contained thiosulfate.

The matrix ions, thiosulfate, trithionate and/or tetrathionate in gold thiosulfate samples had a detrimental effect on the chromatography of this complex. Samples containing thiosulfate caused a memory effect in the chromatographic system, with the thiosulfate content of the preceding sample influencing the gold peak area of the next injection. Low concentrations of thiosulfate in the sample caused increased but irreproducible gold thiosulfate peak areas. These difficulties again could be minimised by the addition of thiosulfate to the eluent. In contrast, the

presence of high (>10 mM) sample thiosulfate concentrations caused a sharp decrease in the gold peak area. This matrix induced a broadening effect with the retention factor of part, if not the entire quantity of the gold complex in the injected sample reduced. The collected experimental data suggested that this was, in part, attributable to a "sample-induced micro-gradient" self-elution effect. Partial recovery of the peak, achieved through adding the eluent ion-interaction reagent to the sample, indicated that the disturbance of the column equilibrium by samples containing high matrix ion concentrations also played some role in the poor chromatographic properties observed for the gold complex. Markedly different results observed when using a polymer-based, compared to a zirconia-based, column for the separation suggested the stationary phase itself may also contribute to these problems.

Low millimolar concentrations of trithionate and tetrathionate in the sample resulted in splitting or broadening of the gold thiosulfate species in the chromatogram. The cause of this has not been determined, but may relate to equilibria between thiosulfate and the polythionates, or could also be caused by the micro-gradient self-elution effect mentioned earlier. In contrast, the addition of 1 M ammonia to gold thiosulfate standards had no significant effect on its chromatography, presenting further evidence that the gold diammine complex is not formed significantly in gold leach solutions.

Separation of the polythionates and the gold thiosulfate complex can be accomplished by the use of a system consisting of a Dionex NG1 and NS1-5μ column in series and an eluent containing 15% *v/v* acetonitrile, 3 mM TBAOH

and 2.5 mM sodium carbonate, with the acetonitrile concentration stepping to 28% *v/v* at injection. Varying the carbonate concentration of the eluent altered the selectivity of the gold thiosulfate peak relative to the polythionates. However, determination of gold thiosulfate in leach solutions was not possible by this technique, which was attributed primarily to the self-elution effect described previously for high thiosulfate containing solutions. The polythionates ($S_xO_6^{2-}$, x = 3 to 5) can be determined using the optimised methodology in a leachate containing 0.5 M $(NH_4)_2S_2O_3$, 2 M NH_3 and 0.05 M $CuSO_4$, without dilution. The chromatography of copper in this system was complicated, with results demonstrating that some on-column precipitation occurred, whilst the fraction remaining in solution appeared to be divided between labile complexes, presumed to contain ammonia and/or thiosulfate as ligands that produced poorly shaped chromatographic peaks.

Thiosulfate, the polythionates ($S_xO_6^{2-}$, x = 3 to 5), and the gold thiosulfate complex could be separated in standards by CE employing 75 μm a fused-silica capillary, a –30 kV applied voltage and an optimised electrolyte containing 25 mM bis-tris adjusted to pH 6.0 with H_2SO_4. The presence of low millimolar concentrations of thiosulfate and the polythionates in the sample was detrimental to gold thiosulfate migration, with irreproducible peak areas and shape resulting, along with peak splitting. This behaviour prevented determination of the gold in leach solutions using this method. However, the CE procedure did provide a rapid alternative methodology for the determination of thiosulfate and the polythionates in leach solutions, although significant dilution of the sample was required prior to injection.

ITP provided an alternative electromigrative technique for the determination of thiosulfate and sulfate in gold thiosulfate leach solutions, with a significantly lower dilution being required than for CE. Using a leading electrolyte of 120 mM bis tris, 20 mM TBACl, 0.05% *w/v* HPMC, adjusted to pH 6.4 with hydrochloric acid, and a terminating electrolyte of 20 mM bis-tris, adjusted to pH 6.4 with formic acid, determination of thiosulfate concentrations up to 0.2 M and sulfate concentrations up to 68 mM was possible in synthetic leach solutions. Detection limits were 2.1 mM for thiosulfate and 1.3 mM for sulfate. To obtain acceptable reproducibility an internal standard (thiocyanate) was required. The developed method also indicated potential for the first simultaneous analysis of the four important non-metal sulfur-oxygen anions in gold thiosulfate leach solutions, namely, sulfate, thiosulfate, trithionate and tetrathionate. The concept of using a singe-capillary mixed ITP/CE system without counterflow for the separation of thiosulfate and the polythionates was demonstrated. Significant difficulties with reproducibility must be overcome before this technique can be used for the determination of anions in high ionic strength matrices, such as thiosulfate leach solutions.

Finally, it should be noted that further work is required in the following areas:

The effect of dilution and any other sample pre-treatment methods on the speciation of the leachate needs to be quantified accurately to establish formally if these procedures introduce any significant inaccuracies into the collected data.

Problems preventing successful chromatographic and electrophoretic determination of the gold thiosulfate are yet to be overcome. Future experiments should focus on developing further understanding of the mechanisms affecting the behaviour of this species. Such work may provide the way forward in developing a technique that can simultaneously determine the gold complex and the other sulfur-oxygen species important to the leach process. The speciation of the other metals, for example copper and silver, that may be present in leach solutions also requires investigation, although work conducted in the present study on the behaviour of the copper complexes suggests that this will be an even more challenging undertaking than the determination of the gold complex.

For the ion-interaction methodology developed for polythionate analysis, the cause of the shoulder on the tetrathionate in leach samples needs to be determined. Finding a means for decreasing the analysis time, without sacrificing the capability to inject undiluted samples, or compromise the detection capabilities of the method, would also be an advantage.

Further method development by CE should focus on shortening the total analysis time and finding ways of reducing the pre-analysis dilution required for the leach samples. The latter problem is however one of the limitations inherent in the use of CE, although development of the single capillary ITP/CE system, demonstrated conceptually in Chapter 6, may offer some advantages for leach samples. An investigation relating to the determination of the gold thiosulfate complex by CE would be to examine the effect of adding thiosulfate to the electrolyte, in a similar fashion to the approach used in the ion-interaction work.

The utility of ITP for gold thiosulfate leach solutions warrants further investigation. The developed method may allow simultaneous determination of the key non-metal sulfur-oxygen species in leach solutions, with the additional advantage that minimal dilution would be required prior to analysis. The use of instrumentation specifically designed for ITP may also result in improvements to the method outlined in Chapter 6, potentially removing the need for an internal standard in the samples. Coupled capillary techniques, particularly ITP-CE, should also be examined in detail for their applicability to leach matrices.