STUDIES ON HPLC TECHNIQUES FOR STRETFORD LIQUORS

A STUDY TOWARDS THE TOTAL ANALYSIS OF STRETFORD LIQUORS USING HPLC TECHNIQUES

by

ANDREW P. HANTA, B.Sc (Honours)

A Thesis

Submitted to the Faculty of Graduate Studies

In Partial Fulfillment of the Requirements

for the Degree

Master of Science

McMaster University

December, 1986.

To

my family,

Who gave me the will to learn and

the encouragement when I needed it the most.

May God bless them always.

MASTER OF SCIENCE (1986)

McMaster University
Hamilton, Ontario

TITLE: A Study Towards the Total Analysis of Stretford Liquors Using HPLC Techniques.

AUTHOR: Andrew Paul Hanta, HBSc. (University of Western Ontario)

SUPERVISOR: Dr. O.E. Hileman Jr.

NUMBER OF PAGES: xiii, 149

ABSTRACT

The ultimate objective of this research project was to establish an HPLC method that allows the quantification of most of the major components of a circulating Stretford process liquor using one sample. The criteria that had to be met were reasonable retention times, resolution approaching 1.0 and quantitative results (ie. with an uncertainty in the accuracy and precision of the results less than $\pm$ 10%). Ion chromatography was the route chosen since the major components of the circulating liquors are present as either inorganic or organic anions. Ion pair chromatography and ion exchange chromatography were the general methodologies investigated during the study.

Ion pair chromatography, specifically soap chromatography, was successful in the isolation of the NaSCN, Na_2SO_4 and $Na_2S_2O_3$ species of the circulating Stretford liquors. It was unsuccessful in the quantitative separation of these species. The method was abandoned in order to find a method which could quantify these species as well as the other components of the circulating liquors.

The ion exchange chromatography studies fell into two categories, that being columns with a silica based packing and columns with a polymer based packing. The

silica based columns had a limited operating range of pH for the analysis and the backbone of these columns degraded at pH values exceeding pH 5.5. The polymer based ion exchange columns had a much wider operating pH range and allowed for the analysis of the Stretford liquors without the need to change the pH of the solution.

The best possible method of analysis was the polymer based technique. All of the components of the Stretford liquors, with the exception of the ADA (anthraquinone disulfonic acid) could be quantified in under 15 minutes. The method provided quantitative results and very good resolution between the species eluted.

ACKNOWLEDGEMENTS

I would like to thank Dr. Hileman for his advice and guidance in the course of this research project. I would also like to thank Michael Malott for his assistance and Diane Johnson for the many refreshing morning conversations.

Furthermore, I would like to acknowledge the financial assistance of the Chemistry Department.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1

INTRODUCTION

CHAPTER 1

INTRODUCTION

1.1 Setting

The Stretford process is a liquid redox desulfurization technology used for the removal of hydrogen sulfide from sour gas streams. A typical process flow diagram is illustrated in Figure 1.1. It is an alternative to the Claus process which involves the conversion of the H_2S to elemental sulfur and steam by reduction with oxygen. The Stretford process is a less capital intensive technology that can be applied directly. Thus, it is being considered in the synthetic fuel area as a possible scrubbing technique.

The Stretford process basically involves the absorption of H_2S into a circulating, aqueous base followed by the oxidation of HS^- to S^o through a redox reaction involving the reduction of V^{5+} to V^{4+}. The HS^- forms solid sulfur and water at this stage. In a separate vessel, the V^{5+} is regenerated through the use of dissolved oxygen in the presence of anthraquinone disulfonic acid (ADA). Depending on the composition of the feed gas stream and on operating conditions, various by-product ions can form in solution, as well. Regular on line analysis of process liquors could provide the information required for process

monitoring, and process control and optimization. No such analytical methodology is available.

1.2 Overview of Current Analytical Methodologies for Stretford Process Analyses

A Stretford process assay is comprised of many parts. In order to do a full analysis the following streams must be considered: the sour gas feed, the exiting sweet gas, oxidizer vent gas, the melt tank vent gas, the liquid waste, the solid waste, the product sulfur and the circulating liquors. In order to obtain a better understanding of the chemistry of the Stretford process precise and accurate quantitative methods for the analysis of the circulating liquor are necessary. Presented here is a review of past and present methods commonly used to determine the composition of the circulating Stretford liquors.

Virgin Stretford liquors are composed of $Na_2CO_3/NaHCO_3$ (25.0 g/L as Na_2CO_3), $NaVO_3$ (1.5 g/L as V), trisodium citrate dihydrate (10.0 g/L) and sodium anthraquinone disulfonate (commonly known as ADA)(3.0g/L). Ideally, the ADA should be the 2,7- isomer but an isomer mixture is more commonly encountered. It is usually composed of the 2,6- and 2,7- isomers, with varying amounts of the 1,5-, 1,6- and 1,7- isomers present as well.

When H_2S is passed through the Stretford liquor, the end products are ultimately solid sulfur and water. The solution is deep red to brown in color. Intermediate

species, such as polysulfides, and various by-products are formed, however. The most common by-products are Na_2SO_4 and $Na_2S_2O_3$. The concentration of each range up to the solubility limit. If hydrogen cyanide is present in the feed gas stream, NaSCN will also be produced. Most suites of analytical methodologies for the Stretford process quantitatively analyze for all of the compounds noted thus far. In as much as the analytical methodologies for the Stretford process were established in the early to mid sixties for use as quality control techniques in the coke making industries, the method development approach taken was based on classical techniques.

The standard method for the determination of the Na_2CO_3 and $NaHCO_3$ was developed by W.C. Holmes Ltd. (now Peabody Holmes Ltd.).[1] The Stretford liquor is titrated against a standard H_2SO_4 solution with a pH meter indicating the endpoint. The endpoint used is either that of methyl orange, known as M-alkalinity, or that of phenolphthalein, known as P-alkalinity. Methyl orange has a pKa of 3.46 and a pH transition interval between 3.1 and 4.4. Phenolphthalein has a pKa of 9.5 with a pH transition range from 8.0 to 9.8. The respective endpoints indicate the carbonate bicarbonate reactions:

$$H^+ + HCO_3^- \quad ---> \quad H_2CO_3 \quad \text{for methyl orange}$$

$H^+ + CO_3^{2-} \longrightarrow HCO_3^-$ for phenolphthalein

Whether chemical indicators are used or not, the method has drawbacks in addition to the visual interference with the chemical endpoints. Other species are being titrated as well as evidenced by a large buffer capacity at pH 9.35. Interferences can result from a proton from citric acid which has pKa values of 3.13, 4.76 and 6.40. The vanadates can also participate in proton transfer reactions. Depending upon the pH of the solution a variety of reactions can take place with the vanadium. Possible species are $V_6O_{17}^{4-}$, $V_4O_{12}^{4-}$, $V_3O_9^{3-}$, $H_nV_2O_7^{(4-n)-}$, $V_2O_7^{2-}$, HVO_4^{2-}, VO_4^{3-} which occur at different pH's over the entire pH range.[2] A few of the possible reactions are:

$$2H_2O + VO_4^{3-} + H^+ \longrightarrow [VO_3(OH)(H_2O)_2]^{2-}$$

$$2[VO_3(OH)(H_2O)_2]^{2-} \longrightarrow V_2O_7^{4-} + 5H_2O$$

$$2[VO_3(OH)(H_2O)_2]^{2-} + H^+ \longrightarrow HV_2O_7^{3-} + 5H_2O$$

$$[VO_3(OH)(H_2O)_2]^{2-} + HV_2O_7^{3-} + 2H^+ \longrightarrow V_3O_9^{3-} + 4H_2O$$

$$2V_3O_9^{3-} + 2H^+ \longrightarrow V_6O_{17}^{4-} + H_2O$$

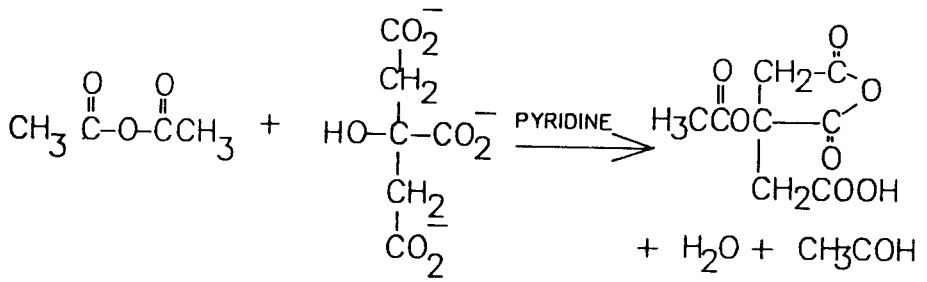
There is also the possible participation of the by-products in proton transfer reactions. Typical pKa's are as follows[3]:

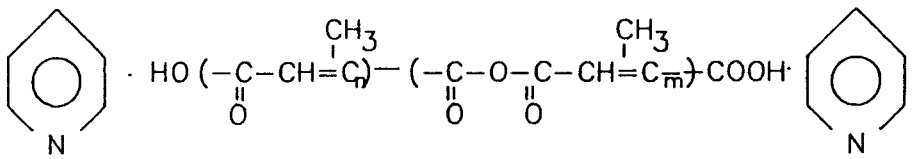
Compound	pKa
HSCN	-1.85
$H_2S_2O_3$	1.74

Compound	pKa
H_2SO_4	-3, +1.96
H_2SO_3	1.89, 7.21
H_2S	7.05, 14.0
H_2S_3	-1.00
HS_4^-	7.00
HS_5^-	6.10

The pKa's of these by-products are in the range to allow for proton transfer. The method is claimed to be accurate to $\pm$ 0.53 g/L Na_2CO_3 and to $\pm$ 0.84 g/L $NaHCO_3$.

The most common method used for the determination of the tri-sodium citrate dihydrate has also been developed by Peabody Holmes Ltd.[4] It is a colorimetric technique in which the citrate ion is reacted with acetic acid in pyridine. Two mL of the Stretford liquor are reacted with 5 mL of concentrated H_2SO_4 in order to remove the sulfides as H_2S and to remove the carbonates as CO_2. This is then diluted to 100 mL with H_2O. One mL of this solution is then added to 1.3 mL pyridine and 5.7 mL acetic anhydride at 32C. The reaction proceeds through acetocitric acid γ-anhydride which, in the presence of pyridine, gives a red color visible at 420 nm. Ultimately, a polyvinyleneketo-anhydride is formed with pyridine which also gives this red color. The reaction sequence follows[5]:





This is a very temperamental method in that the quality of the control of the temperature and laboratory technique greatly affect the repeatability of the results obtained. If proper care is not taken, the reaction will not go to completion. Furthermore, the reaction is not very specific since other compounds which may have hydroxyl groups or double bonds can react in a similar manner. Interference from vanadium species can be prevented by the addition of NaSCN, if not originally present. This method is claimed to be accurate to $\pm$ 0.5 g/L tri-sodium citrate dihydrate. It is, however, very labor and time intensive requiring upwards of 30 minutes for each analysis.[6]

In the wet chemical analysis of vanadium the first method to be considered is recommended both by Peabody Holmes Ltd.[7] and the British Gas Corporation.[8] It involves a redox titration. The indicator used is Analoid, a commercial name for sodium diphenylamine sulfonate. The Stretford solution is first acidified to remove the sulfur species and carbonate.

$$\left.\begin{matrix} CO_3^{2-}, S_2O_3^{2-} \\ \text{polysulfide, } HS^- \end{matrix}\right\} + H^+ \longrightarrow \left\{\begin{matrix} S + SO_4^{2-} + H_2S \\ + CO_2 \end{matrix}\right.$$

The vanadium is oxidized to V^{5+} with $KMnO_4$.

$$H_2O + 5VO^{2+} + MnO_4^- \longrightarrow Mn^{2+} + 5VO_2^+ + 2H^+$$

The V^{5+} is then reduced with Fe^{2+} as titrant.

$$2H^+ + VO_2^+ + Fe^{2+} \longrightarrow Fe^{3+} + VO^{2+} + H_2O$$

The method is claimed to be accurate to $\pm$ 0.02 g/L of vanadium.[6] Possible interferences result if the H_2S, polysulfide and thiosulfate are not completely removed. This method has drawbacks. When operating on the laboratory or bench scale 50 mL of Stretford liquor may be a considerable fraction of the total liquors to use for one analysis. Furthermore, the method is very labor and time intensive requiring 30 minutes for each analysis.

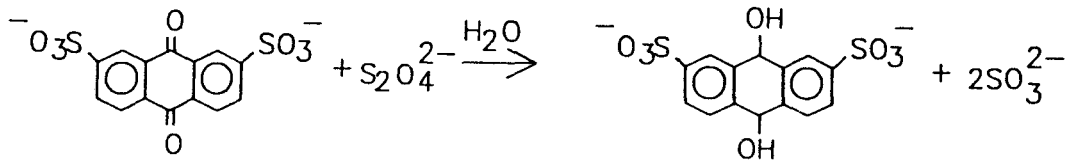
An extraction technique that allows for the selective determination of V^{5+} has been established by Thornton, of McMaster University.[9] With this method the V^{5+} is selec-

tively extracted into trioctyl phosphine oxide from the Stretford liquors. It is then stripped from the trioctyl phosphine oxide by a liquid-liquid extraction technique using 0.5 M Na_2CO_3. The optical density of the solution is measured at 690 nm. Problems arise since at best only 87% $\pm$ 5.5% of the V^{5+} is extracted. Furthermore, the presence of SCN^- and CO_3^{2-} decreases the ability of the trioctyl phosphine oxide to extract the V^{5+} from the liquors. The results tend to be on the low side. They are repeatable, however. Thus, one can run standards to correct for these deviations.

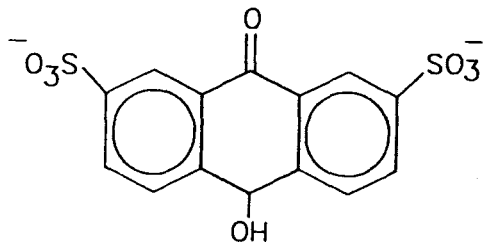
A potential new method based on an extraction and the formation of an organic complex with the V^{5+} has been developed by Shcherbakova, et. al..[10] A spectrophotometric finish is used. There are many complexes which can be formed and detected using a UV/Visible spectrophotometer. In this particular case the vanadium forms a complex with 1-phenyl-3-methyl-4-benzoylpyrazolone-5 (PMBP) in n-pentanol. The V^{5+} can be detected in the presence of V^{4+} using this method. It is potentially useful method since it shows high sensitivity and allows for quick analysis.

To analyze for the ADA, Peabody Holmes Ltd. recommends the reduction of it to anthrahydroquinone with $Na_2S_2O_4$ followed by a spectrophotometric finish.[11] The reaction is

monitored at 440 nm or 445 nm using a spectrophotometer and is as follows:



Very little Stretford liquor is required for the assay (5 mL). The method is claimed to be accurate to ± 0.2 g/L and the time for analysis is roughly 15 minutes.[6] Possible errors could arise from the incomplete reaction of the ADA and by-products could result. These other species would probably absorb in the same region as the anthrahydroquinone. One potential by-product of this reaction could be:



The response factors for the various sulfonate isomers are different from each other and this could affect the resulting absorbance. Other, though unlikely interference at 440 nm or 445 nm could result from citrate or the vanadate. The by-products such as sulfide (HS^- Λ_{max}:230 nm) (where Λ_{max} is

the absorption maximum), thiosulfate (Λ_{max}:215 nm) and thiocyanate (Λ_{max}:240 nm) all absorb at low wavelengths. Typical absorbances for the polysulfides are as follows[12]:

Species	Λ_{max}(nm)
SS^{2-}	410
S_2S^{2-}	416,333,286
S_3S^{2-}	416,367,303

The above could very likely interfere at 440 nm or 445 nm. As a note, one generally observes a decrease of ADA concentration in the solution as the liquor is used but this does not seem to affect the functional ability of the solution.

A potential technique to be considered is infrared spectroscopy. This technique has been used to quantify the 2,6 ADA isomer since 1982. KBr pellets are formed and at wavelengths 10.35 µm and 10.75 µm transmissions are taken. These are converted to weight percent 2,6-ADA by calibration curves. It should be noted that the error associated with quantitative IR is usually very large.

By-product analysis has generally focussed on traditional methods. Peabody Holmes Ltd. analyzes for NaSCN using a colorimetric technique.[13] Very little Stretford liquor is needed and a 1:500 dilution is usually done. $FeCl_2$ is added to 10 mL of the solution and an $Fe(SCN)_2$ complex is formed.

$$FeCl_2 + 2SCN^- \longrightarrow Fe(SCN)_2 + 2Cl^-$$

This complex is detected spectrophotometrically at 470 nm. The reaction has drawbacks since it is not stable in bright light. Thus, the reaction should be quickly carried out. Possible by-products could be FeS_2O_3, $FeSO_4$ and even a vanadium complex with the iron, however, the sulfate and thiosulfates can not be detected spectrophotometrically. The advantages of this method are that very little Stretford liquor is needed (1 mL) and the method is quick, requiring only 10 minutes. One disadvantage of this method is that it is repeatable only to $\pm$ 4.0 g/L.[6]

A common method for the analysis of Na_2SO_4 involves the acidification of the Stretford liquors to remove the carbonates and any sulfides.[14]

$$HCO_3^- + H^+ \longrightarrow H_2O + CO_2$$

$$2H^+ + S^{2-} \longrightarrow H_2S$$

Formaldehyde is added to remove sulfite interference and iodine is added to remove thiosulfate interference.

$$NaHSO_3 + H_2CO \longrightarrow H_2C(OH)SO_3^-Na^+$$

$$2S_2O_3^{2-} + I_2 \longrightarrow S_4O_6^{2-} + 2I^-$$

The sulfate is then precipitated out of solution as $BaSO_4$.

$$BaCl_2 + SO_4^{2-} \longrightarrow BaSO_4 + 2Cl^-$$

The $BaSO_4$ is filtered off, dried and weighed. Interferences could arise from unreacted thiosulfate ion reacting with the

barium. Likewise, the sulfite ion and sulfide ion could also react with the barium and precipitate out of solution if not adequately removed. There rests a possibility that the vanadium could react with the barium and form a precipitate. The method is accurate to ± 3 g/L and the analysis time, that is for the operator, is said to be 5 minutes.[6] The actual time for the reaction takes upwards of twelve hours.

An indirect method to determine Na_2SO_4 follows on from the determination of soluble fixed sulfur.[15] The fixed sulfur technique allows for the determination of the total amount of sulfur in the liquors. The Stretford liquor is reacted with NaOCl to oxidize the sulfoxy anions to sulfate.

$$S^{2-} + 4OCl^- \longrightarrow 4Cl^- + SO_4^{2-}$$

Any excess hypochlorite ion is decomposed with HCl.

$$H^+ + HCl + OCl^- \longrightarrow Cl_2 + H_2O$$

A measured amount of $BaCl_2$ is added to react with the sulfate.

$$BaCl_2 + SO_4^{2-} \longrightarrow BaSO_4 + 2Cl^-$$

The excess barium is then back titrated with EDTA using Eriochrome black T as the indicator. The Na_2SO_4 is determined as the result after subtracting the NaSCN and $Na_2S_2O_3$ which have been determined by other methods. This method is presently used by Peabody Holmes Ltd. It has many draw-

backs. If the dissolved salt concentration is small then upwards of 250 mL of Stretford liquor are needed in order to determine the Na_2SO_4 concentration. The method is accurate to $\pm$ 0.6 g/L and the approximate analysis time is 60 minutes.[6]

The determination of total dissolved salts is an important technique in by-product analysis. This method is also used by Peabody Holmes Ltd.[16] It basically involves the collection of 10 mL of Stretford liquor, filtration and then evaporation overnight at a temperature of 150 C. This method is accurate to $\pm$ 1% of the recorded total dissolved salt.[6]

Some work is presently being carried out using Raman spectroscopy as a possible technique to quantify the by-products.[17] An argon ion laser has been used with a slit width ranging from 5.6 cm^{-1} to 27.8 cm^{-1}. It has a detection limit of 8.64 to 8.97 g/L. A drawback to this method is the high capital cost involved with the Ar^+ laser and the temperamental nature of present laser technology, thus, limiting its scope in routine analytical chemistry.

The most common method used for the determination of $Na_2S_2O_3$ involves a back titration.[18] It has been recommended by Peabody Holmes Ltd. It is an I_2 titration where thyodene powder has been added and one titrates the excess

iodine with $Na_2S_2O_3$. The drawbacks to this method are that it is labor and time intensive requiring 20 minutes for each analysis. Interference problems can result from the V^{5+} which will oxidize the I_2. Thus, hydrazine is added prior to the addition of the I_2 to reduce the V^{5+} to V^{4+}. This method is accurate to $\pm$ 0.3 g/L.[6]

Thus, traditional methods are time consuming and labor intensive. No significant attempt has been made to analyze various components of the circulating liquors from one sample. Since these methods are based on wet chemical techniques the possibilities of various sources of contamination and error arise. This could and does effect the accuracy and the precision of the results currently obtained.

1.3 Some Potential Rapid Analytical Methodologies for the Analysis of the Stretford Liquors

Chromatography, in particular HPLC seems to be the most reasonable route to take to analyze for the various components of the Stretford liquors. Since all of the major Stretford components exist as either inorganic or organic anions with the charge balance being provided, primarily, by sodium ions, two possible chromatographic routes exist.

They are ion pair chromatography and ion exchange chromatography.

1.3.1. Ion Pair Chromatography

The principles behind ion pair chromatography rest in liquid-liquid extraction techniques. Ion pairs are created using an appropriate counter ion. The counter ion should have a long enough alkyl chain to allow for interaction with the organic phase while maintaining enough ion character to allow for interaction with the species being investigated or separated.

$$A^+_{aq} + B^-_{aq} \longrightarrow AB_{org}$$

The ion pair will then favor the organic phase and thus a phase equilibrium is facilitated. Since the ion pairs are nonionic, they can be separated using either reversed phase or normal phase chromatography techniques. The extent to which these ion pairs are retained on the column is determined by many factors. One primary factor to be considered is the degree of polarity of the ion pair formed for reversed phase columns. A more polar ion pair will have a greater affinity for the stationary phase and, thus, a longer retention time.

An important variable involved in a separation is the capacity factor, k'. It is defined as the ratio of the number of moles of solute in the stationary phase relative

to the number of moles of solute in the mobile phase. It is also related to the retention times of the eluting species relative to the retention time of the solvent front

ie. $k' = (t_R - t_o)/t_o$

where t_R: retention time of species

t_o: retention time of solvent front

It can also be expressed as

$k' = K_D(V_{stat.}/V_{mob.})$

where K_D is the equilibrium constant defined as:

$K_D = [conc]_{stat.}/[conc]_{mob.}$

$V_{stat.}$ = volume of stationary phase

$V_{mob.}$ = volume of mobile phase

The selectivity, or separation factor, α, is another important variable to be considered and is defined as the ratio of the capacity factors for two adjacent peaks.

ie. $\alpha = k'_2/k'_1$

This ratio is so defined that the range of α values rests between one and infinity with a better resolution resulting from higher α values. In ion pair chromatography the mobile phase will be defined as the mixture of two components. They are the organic stock solution and the aqueous stock solution. The organic stock solution is only composed of methanol in this work whereas the aqueous stock solution is composed of water, the buffer solution ($HPO_4^{2-}/H_2PO_4^-$) and the ion pair reagent (either cetyl trimethylammonium bromide

(CTMA) or tetrabutylammonium hydroxide (TBA)). This is illustrated in Figure 1.3.1. Adjustment of the pH, the mobile phase elution strength, the surface tension, the type of stationary phase used and the temperature used in a separation will allow for improvement in the selectivity, resolution and column efficiency obtained in multicomponent separations.[19]

Reeve, of Peabody Holmes Ltd., developed one of the early methods to determine ADA using a reversed phase HPLC technique.[20] He used a Sil 60-D 10-CN column (25 cm by 4 mm) with a combination of methanol and an aqueous buffer comprised of 0.1 M Na_2HPO_4 and 0.1 M KH_2PO_4 as the eluent. A long alkyl chain in the ion pairing reagent ensured that there was sufficient interaction with the stationary phase. Reeve attempted to use two different ion pairing reagents. They were cetyl trimethylammonium bromide (CTMA) and tetrabutylammonium hydroxide (TBA) each at a concentration of 0.1% w/v. A typical reaction with the anions investigated would be the following.

$$R_4N^+Br^- \quad ---> \quad R_4N^+ \quad + \quad Br^-$$

$$R_4N^+ \quad + \quad ADA^{2-} \quad ---> \quad [ADA^{2-}(R_4N^+)_2]$$

This ion pair complex would then interact with the stationary bonded phase. A UV detector at 254 nm was used to detect the ion pairs.

Reeve had limited success, however. When TBA was used as the ion pairing reagent the retention time for the prominent 2,7-ADA isomer was 37 minutes and the retention time for the other isomers greatly exceeded 37 minutes. CTMA provided a much more realistic retention time for the 2,7-ADA isomer. It eluted at 18 minutes with the other isomers following there after. When analyzing for NaSCN and $Na_2S_2O_3$ the UV detector was set at 215 nm to allow for the low wavelength absorbances of these species. TBA proved to be unsuccessful for both the NaSCN and the $Na_2S_2O_3$ with the NaSCN eluting at 13 minutes and the $Na_2S_2O_3$ eluting with the solvent front. Greater success was encountered with the CTMA as the ion pairing reagent. Retention times of 3 minutes and 2 minutes were noted for the NaSCN and the $Na_2S_2O_3$ respectively.

Other limitations to this technique were extensive tailing and poor peak shape with the thiosulfate peak. Reeve was unable to detect Na_2SO_4 using a UV detector since no chromophores were present. Thus, his technique was limited to the detection of only the thiosulfate and the thiocyanate anions found in the circulating Stretford liquors along with ADA and ADA isomers.

Others have also attempted to use ion pair techniques to quantify the ADA isomers. Union Oil used a 10 µm

Spherisorb ODS column (250 mm by 3 mm).[21] They used TBA, also, as the ion pairing reagent and used a fixed wavelength (254 nm) UV detector. They claimed to have success in the separation of the 2,7-ADA isomer. An accuracy of 3% and precision of 3% were reported for the 2,7 isomer. The accuracies for the other isomers were in the range of 10%. Pure standards of all the isomers are difficult to obtain, thus, calibration was difficult to carry out.

The North West Gas Board has also developed an ion pair technique to analyze ELVADA samples (an industrial name for a commercial isomer mix of ADA).[22] A Hypersil-5μm ODS column was selected and used. Again a fixed UV detector was used and their eluent was a combination of acetonitrile and water with CTMA as the ion pairing reagent. This method is relatively new (September 1985) and little data are available as to the quality of the method.

From the above results, one can conclude that ion pair chromatography has a limited scope. At best only three of the possible seven components of the Stretford liquors can be separated let alone quantified. Furthermore, the detector must be adjusted from 215 nm to 254 nm to facilitate detection of the ADA. Thus, in order to simultaneously detect the three species present two detectors must be used which naturally increases the dead volume and, thereby,

results in peak broadening as well. A conductivity detector would be an alternative to a two detector system provided that the background conductivity could be suppressed.

With this limited success in ion pair chromatography it was thought wise to investigate ion exchange chromatography.

1.3.2. Ion Exchange Chromatography

There are basically two types of systems used for ion exchange chromatography, suppressed and non-suppressed. In anion analysis, suppressed systems use a low capacity anion exchange column to separate the anions. A second column with a strong cation exchanger then reduces the conductivity of the mobile phase.

In ion exchange chromatography the mobile phase or eluent consists of an aqueous stock solution. This stock solution consists of water and an eluent anion such as the phthalate anion and its appropriate counter ion. This is illustrated in Figure 1.3.2.

Consider the eluent anion to be aqueous NaOH and the samples to elute as halogens, X^-. The reactions in the separating column are

$$Resin\text{-}NR_3^+OH^- + Na^+X^- \longrightarrow Resin\text{-}NR_3^+X^- + Na^+OH^-$$

and in the suppressor column

$$Resin\text{-}SO_3\text{-}H^+ + Na^+OH^- \longrightarrow Resin\text{-}SO_3^-Na^+ + H_2O$$

$$Resin\text{-}SO_3\text{-}H^+ + Na^+X^- \longrightarrow Resin\text{-}SO_3^-Na^+ + H^+ + X^-$$

The eluent anion, OH^-, is converted to a neutral species, H_2O, by the suppressor column and the only anion left to detect is that of the halogen, X^-. Thus, the conductivity of the eluate is eliminated and the conductivity signal is due to only the halogen anion.

Frequent regeneration of the suppressor column is necessary to restore the proton to the SO_3^- sites. This is usually accomplished by flushing the suppressor column with a base to remove the metal cation.

Sunden, et. al. developed a gradient method in 1983 for the separation of SO_4^{2-}, $S_2O_3^{2-}$ and SCN^-.[23] A Dionex system was used with two Dionex precolumns (4 mm by 50 mm) in series serving as the separator column. An Amberlite AG (5.7 mm by 300 mm) column served as the suppressor column. The eluent system started at 4.8 mM $NaHCO_3$ / 4.7 mM Na_2CO_3 and the gradient finished at 7.2 mM $NaHCO_3$ / 9.1 mM Na_2CO_3. The detection system was a Conducto Cell with a Conducto Monitor (LDC). The anions were effectively separated in under 15 minutes, however, the thiosulfate peak did show extensive tailing. A drawback to gradient analysis was the equilibration time needed between sample runs. This allowed for fewer analysis being run per day and increased the cost per analysis.

There were other drawbacks to the suppressed technique. These drawbacks resulted primarily from the suppressor column. One significant problem was the band broadening of the anion peaks which resulted from the added dead volume due to the suppressor column. Another problem encountered was that the suppressor column required periodic regeneration to restore the ion exchange capacity of the column. A third problem was that the eluents which could be used in this system were limited to those which could be readily protonated in the suppressor column itself.[24] Use of a non-suppressed system effectively eliminated these problems.

Non-suppressed systems, generally fall into two categories. Those using high capacity ion exchange materials and those using low capacity resin or silica based ion exchange material. The reactions for either case are as follows:

$$R_3N^+ + E^- \longrightarrow R_3N^+E^-$$

$$R_3N^+E^- + X^- \longrightarrow R_3N^+X^- + E^-$$

where E: eluent anion, X: sample anion

The high capacity ion exchange packings have found limited use with inorganic anion analysis since this high capacity resulted in a strong interaction of the anion with the packing material. Thus, a high ionic strength eluent anion was then necessary to elute the sample anion. A high ionic

strength eluate would result in the conductivity detector being almost useless since the background conductivity is very large, so large that the background signal cannot be electronically suppressed. Therefore, electrochemical, amperometric, UV and post-column reaction detection systems could be used which would generally increase the cost of the detection system.

Schmuckler et. al. in 1979 developed a low capacity resin based anion exchange material.[25] When a low ion exchange capacity resin is used, a dilute eluent with an eluent anion of low conductivity and ionic strength was sufficient to elute the anions. Thus, a conductivity detector could be used which could effectively suppress the eluent conductivity with the electronic suppression available. The eluent anions which Fritz used were aromatic acids such as phthalic acid, benzoic acid and sulfobenzoic acid in concentrations of approximately 1mM. Fritz achieved separations of weakly retained anions such as F^-, Cl^- and Br^-, however, the resin which he used was not capable of allowing better resolution between more complicated matrices.

Silica based low capacity anion exchange materials provided better efficiencies for more complicated matrices. The most common eluent anion used was phthalic acid and it

sufficiently resolved the peaks due to sulfate and thiosulfate in natural water samples. A problem with silica based columns is the limited operating pH range (ie. the silica backbone of the packing material is stable only over a pH range of pH 2 to pH 5.5). Thus, to separate the Stretford liquor anions the liquors must be adjusted from pH 8 to pH 3.5. It was attempted to try and use this technology in the separation of these anions in circulating Stretford liquors.

In 1981 Dogan and Haerdi reported the successful separation of $HCOO^-$, Cl^-, NO_2^-, Br^-, NO_2^-, SO_4^{2-} and $S_2O_3^{2-}$.[26] Dogan used a Vydac 302 IC column (250 mm by 4.6 mm), a precolumn (Wescan 269-003), a conductivity detector (Wescan model 213), an injector (Rheodyne 7125) and a Milton-Roy pump (model 396) with a pulse dampener. The operation temperature was 30° C. With a mobile phase where the eluent was sodium hydrogen phthalate at a concentration of 4 mM and pH 3.9 and at pH 5.1 he was able to resolve the anions in question down to the 0.1 to 0.2 ppm level using a 0.2 mL injection volume. The carbonate peak appeared as a negative peak at pH 3.9 and as a positive peak at pH 5.1. This negative peak could be due to the decreased conductivity of the carbonate relative to the phthalate anion. At low pH the reaction could be

$$HCO_3^- + H^+ \longrightarrow H_2CO_3$$

Thus, a neutral species would decrease the conductivity relative to the eluent used.

Similar success was encountered by Stetzenbach and Thompson in 1983 in their analysis of ground water for Cl^-, Br^-, NO_3^-, I^- and SCN^-.[27] They used a UV detector at 195 nm and had a lower detection limit near to 50 ppb. Stetzenbach and Thompson used a UV detection system since they felt that the conductivity detectors were limited in their sensitivity range (only good to 1.0 ppm) and the detectors are very sensitive to temperature fluctuations. Stetzenbach and Thompson used anion exchange columns such as the Whatman SAX 10 µm (250 mm by 4.6 mm) and a Brownlee 40 mm anion exchange column. The mobile phase system used was 0.15 M KH_2PO_4 buffer. The sample anions were all clearly resolved in 15 minutes or less. They were fortunate in their analysis since all the sample anions which they were interested in had significant absorbances in the range 190 nm to 240 nm.

Cochrane and Hillman showed in 1982 that the UV detector was not limited to the detection of species which absorb light.[28] They showed that by using a UV detector and a highly absorbing eluent anion one could detect species (such as Cl^-, NO_3^- and SO_4^{2-}) which had a much lower or even zero absorbance at a particular wavelength. They used a Vydac 302 anion exchange column and a

UV detector set at 308 nm. The eluent anion which they used was 5 mM KHP. The sample anions detected were non UV absorbing or had a much lower level of UV absorbance than the KHP. (Thus, the sample anions appeared as negative peaks.) The Λ_{max} for KHP was 280 nm, however, 308 nm was used since the zero suppression was not adequate at 280 nm. When compared to the response factor for the conductivity detector the UV detection response was found to be greater by a factor of 5 to 30 depending upon the sample anion investigated. The upper limit of the linear dynamic range also increased for the sample anions investigated. For example the upper limit for SO_4^{2-} was 80 ppm using conductivity and 100 ppm using UV detection. The detection limit also decreased from 3 ppm to 0.3 ppm using a UV detector as opposed to a conductivity detector.

Since some success had been achieved using ion exchange techniques on inorganic anions Mistry, with the suggestion of Peabody Holmes Ltd., attempted to use the technique on the Stretford liquors to determine the vanadium content.[29] He used an Amberlite CG 400(Cl) column in the sulfate form. The column measured 50 cm. He attempted to use various eluent anions at different pH levels. Using 1M $(NH_4)_2SO_4$ at either pH 8.9 or 9.7 he was able to resolve the vanadium and thiosulfate peaks from the solvent front and

from each other. He had similar success using three different eluent anions. He used 1M $(NH_4)_3$citrate at one of three different pH levels (pH 8.0, 8.9 and 9.7), or 1M $NaClO_4$ at pH 8.9 or 1M NaCl. He monitored the UV responses at 254nm and, therefore, was only able to see those sample anions with natural chromophores. Thus, at best he was limited to the detection of possibly $NaVO_3$, $Na_2S_2O_3$, NaSCN and ADA and the isomers of ADA. By using such high concentrations of eluent anions it was impossible for him to use a conductivity detection signal since the background conductivity could not be suppressed electronically using this one column system.

Polymer based anion exchange columns have recently come on the market and show great promise.[30] Since the backbone of the column is a polymer chain rather than a silica chain it can withstand a far greater operating pH range. With the Hamilton PRP-X100 column the working pH range is from pH 1 to pH 13, far more versatile than a silica based anion exchange column which has a working range limited to pH 2 to pH 5.5. This polymer column would be more suitable to the analysis of circulating Stretford liquors since the natural pH of this solution is at approximately pH 8.5 $\pm$1. Thus, lowering the pH of the liquors is not necessary and the sulfoxy anions will not change.

Many mobile phases with different eluent anions at various pH levels can be used. A typical eluent anion used for suppressed systems is $NaHCO_3/Na_2CO_3$ which could now be used for non-suppressed systems. A gradient system allowed Sunden, Lindgren and Cedergren to separate sulfite, sulfate and thiosulfate using a Dionex system.[31] The concentration of the eluent anion was low enough to be suppressed by electronic suppression yet high enough to facilitate a separation. Concentrations ranged from 4.8 mM $NaHCO_3$/4.7 mM Na_2CO_3 to 6.9 mM $NaHCO_3$/8.6 mM Na_2CO_3 as a final concentration. The separation was accomplished in 15 minutes.

A novel mobile phase for the separation of organic and inorganic anions has been suggested by Okada and Kuwamoto.[32] They used a non-suppressed system and potassium hydroxide as the eluent anion. The anions which they separated were F^-, Cl^-, Br^-, NO_2^-, and NO_3^- to a detection limit of 1.5 ppb, 2.5 ppb, 15 ppb, 15 ppb and 15 ppb respectively. They also effectively separated weak organic acids such as benzenesulfonic acid which with a pKa of 0.07 eluted at 5.97 minutes with an eluent anion concentration of 6 mM KOH.

Organic eluent anions such as benzenesulfonic acid, citric acid and benzoic acid showed some promise. Fritz, Du Val, and Barron compared many different organic eluent

anions as to the retention times for various sample anions ranging from Cl^- to NO_3^- to ClO_3^-.[33] These three acids were successfully separated and detected since reasonably low conductances (ie. low background signals) and reasonable retention times (ie. less than 15 minutes) resulted for the above sample anions. The column used was a 500 mm by 2 mm column filled with an unfunctionalized XAD-1 resin. The pH range was low for these separations in the range of pH 3 to pH 4.

The Hamilton Company has reported some work for the PRP-X100 column in the separation of common inorganic anions such as F^-, Cl^-, NO_3^-, HPO_4^- and SO_4^- using p-hydroxybenzoic acid as the eluent anion at pH 8.6. The separation had been carried out in less than 10 minutes. Similar success was shown for the separation of F^-, Cl^-, NO_2^-, Br^- and CN^- in under 6 minutes using 10 mM phenol at pH 10.1.[34]

Waters Scientific has shown some success using a similar anion exchange column for the separation of citric acid using 0.5 mM trimesic acid (1,3,5-benzene tricarboxylic acid) at pH 8.6 in less than 15 minutes.[35] Thus, many possible mobile phases with different eluent anions exist for the separation of some of the components of the Stretford liquors.

1.4 Statement of Problem and Approach to Solution

In the present analysis of the circulating Stretford liquors wet chemical analysis is still the industry standard. A fundamental drawback to the use of wet chemical methods is that a mass balance on the sulfur cannot be accomplished. Also, the results do not lead to a successful charge balance. Additionally, the total dissolved salts results do not equal the results of the combined values of the masses of the salts. The methods give, consistently, sulfur results that underestimate the feed amounts by approximately 15%. Thus, there is a large systematic error in the present analytical techniques. The reliability of the present approach is, therefore, in question. Other drawbacks to wet chemical techniques are that different sample sizes must be used for each analysis, the time per analysis varies and the overall analysis time is relatively long.

Since ion exchange and ion pair chromatography techniques are well established these may be possible routes to investigate in order to reduce the variability and decrease the uncertainty associated with the present techniques. Chromatographic analysis may allow for many of the components of the circulating Stretford liquors to be quantified in the same analysis, thus, reducing the time and

cost for each component. HPLC techniques may also lead to more sensitive detection levels not currently attainable with the wet chemical methods.

Ion exchange techniques may show greater promise than ion pair techniques since both polymer and silica based anion exchange columns are available. This would allow for a much wider pH range to be investigated and could possibly allow one to quantify the components of the circulating liquors at their natural pH.

The goals of this research project were to gain insight into the total analysis of the Stretford liquors using HPLC techniques. Ion pair techniques will be investigated since they showed some success in the analysis of the NaSCN and the $Na_2S_2O_3$ in the Stretford liquors as well as in the analysis of ADA isomers. Ion exchange chromatography will be investigated both at low pH and at higher pH. Low pH ion exchange chromatography will be investigated since water samples containing many of the components of the Stretford liquors have been successfully determined at low pH levels. High pH ion exchange chromatography will be investigated since the pH of the circulating Stretford liquor is at a pH of approximately 8.5 and it would be advantageous to analyze the liquors without the need to adjust the pH. Adjustment of the pH could lead to a change

in the form of the sulfoxy anions.

Figure 1.1 Flow Diagram of Stretford Process.

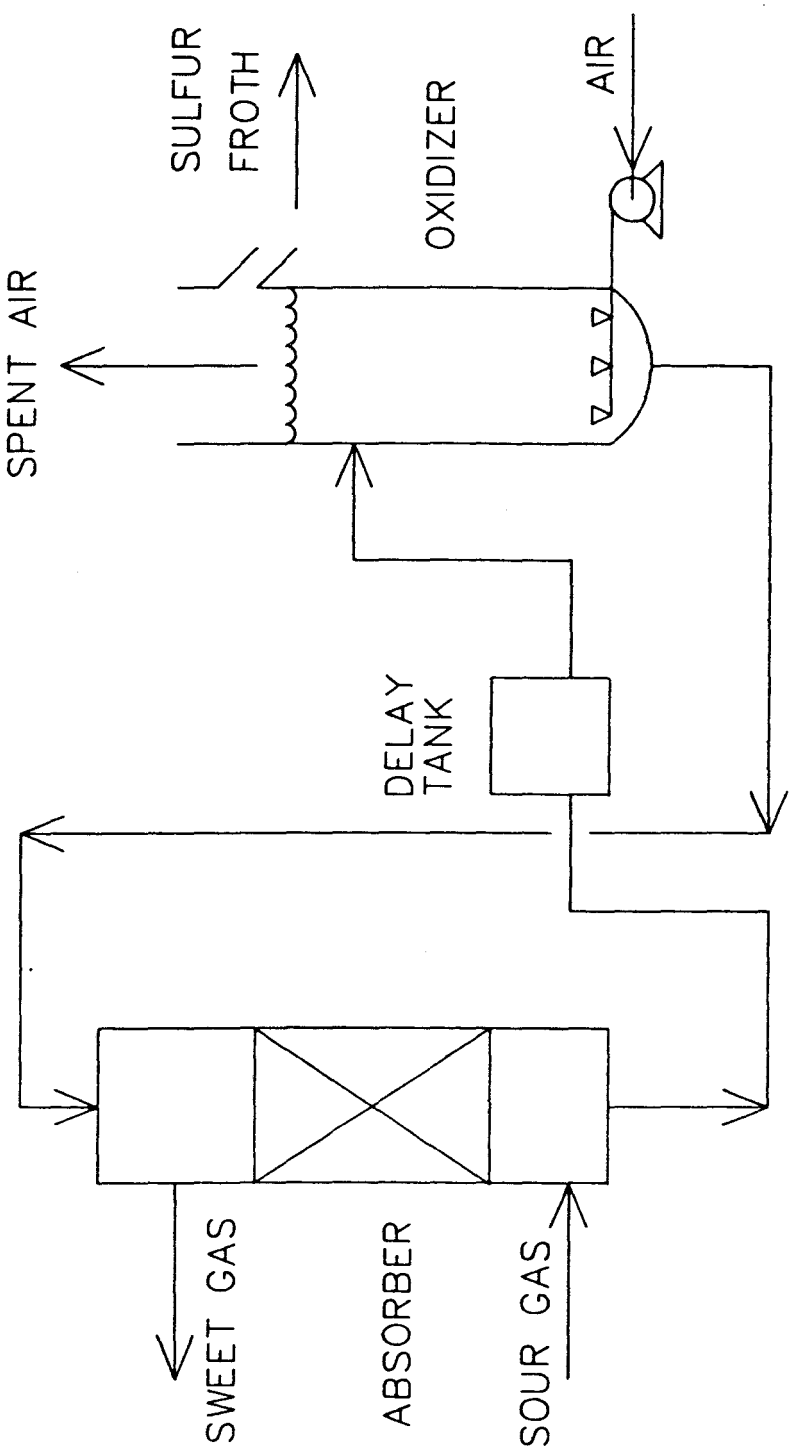

SULFUR
FROTH
OXIDIZER
AIR
SPENT AIR
DELAY
TANK
SWEET GAS
ABSORBER
SOUR GAS

Figure 1.3.1 Mobile Phase Composition for Ion Pair Chromatography.

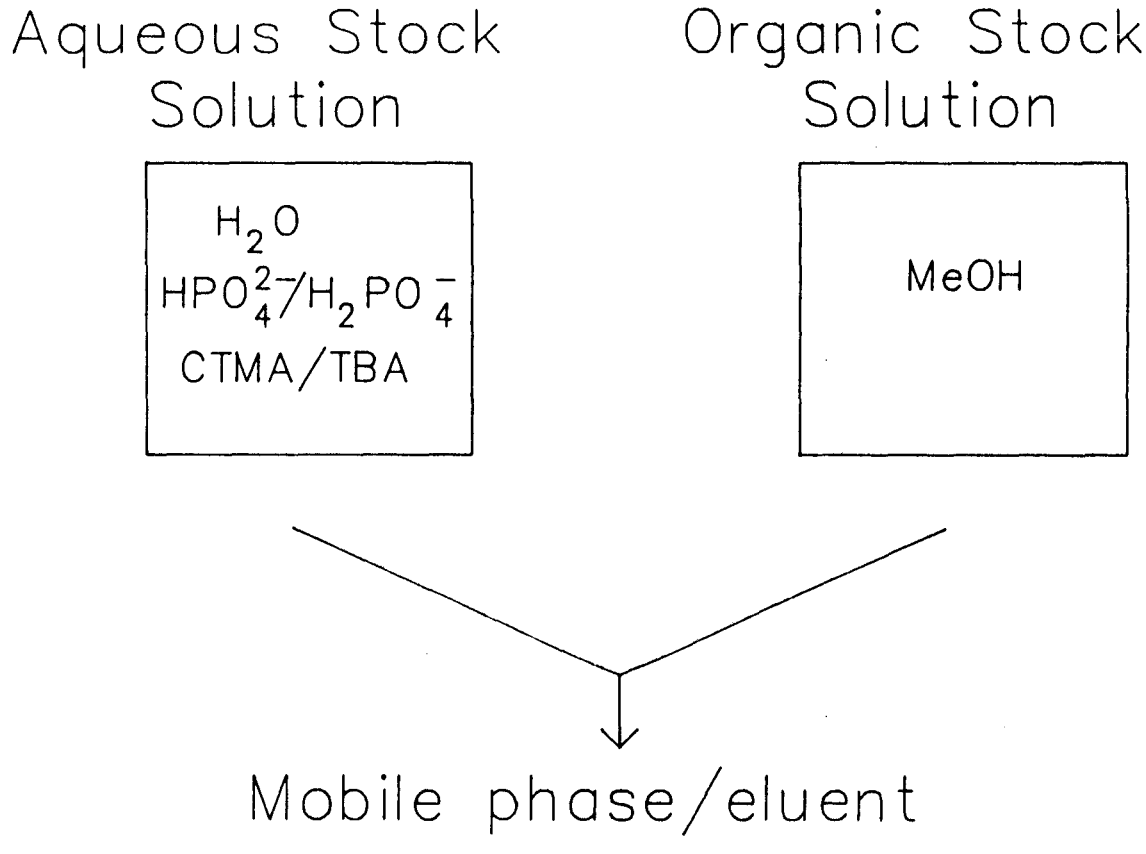
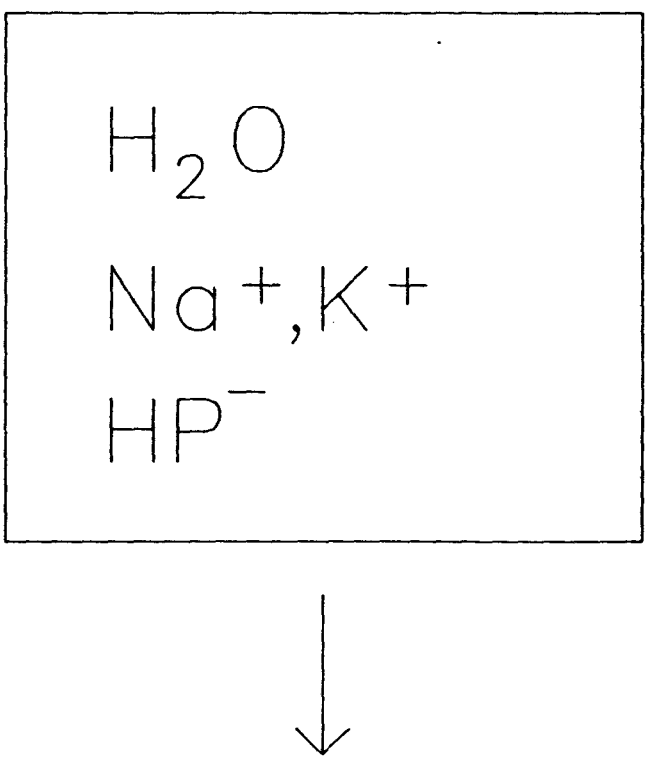

Aqueous Stock Solution
Organic Stock Solution
H_2O
$HPO_4^{2-}/H_2PO_4^-$
CTMA/TBA
MeOH
Mobile phase/eluent

Figure 1.3.2 Mobile Phase Composition for Ion Exchange Chromatography.

Aqueous Stock Solution



Mobile phase/eluent

CHAPTER 2

EXPERIMENTAL DETAILS

CHAPTER 2

EXPERIMENTAL DETAILS

Three different techniques were used in the attempt to separate and quantify the components of the circulating Stretford liquors. These were ion pair chromatography using a Chrompack Sil-60-D-10CN (250 mm by 4.6 mm) column, ion exchange chromatography using a silica based Wescan Anion Column (#269-001) (250 mm by 4.1 mm) and ion exchange chromatography using a polymer based Hamilton PRP-X100 Ion Chromatography column (#70433) (250 mm by 4.1 mm). The difference between the two ion exchange columns rested in the fact that the Wescan column was a silica based ion exchange column whereas the Hamilton column was a polymer based ion exchange column. This allowed for a wider pH range to be studied.

2.1. Ion Pair Chromatography

This technique was used in the separation of the NaSCN, $Na_2S_2O_3$, Na_2SO_4 and the Na_2S. The technique was similar to that used by Pitts[36] for the isolation and separation of the 2,7-ADA and the other isomers.

The eluent consisted of a mixture of methanol and an aqueous buffer solution. The buffer solution was prepared in distilled, deionized water with a concentration of 0.016 M

KH_2PO_4, 0.004 M Na_2HPO_4 and 0.1% (w/v) cetyltrimethylammonium bromide (CTMA). The eluent mixture was 47.5% methanol to 52.5% buffer solution (v/v).

The eluent was combined and filtered through a cellulose acetate membrane filter (pore size 1.0 µm). The eluent was pumped by a single piston, reciprocating, constant displacement pump through the Chrompak column at approximately 1.2 mL/min.. A pulse dampener was connected between the pump and the injection loop valve. A silica precolumn was installed between the pulse dampener and the injection loop.(The guard column was packed with Whatman CO:PELL PAC (#4103-010).) The analytical column, eluent reservoir and conductivity detector were insulated with styrofoam insulation to prevent temperature fluctuations in the conductivity response. A UV detector set at 215 nm was placed in series after the conductivity detector. The sample loop had a volume of 10 µL. The separation was carried out at room temperature.

Samples for analysis were prepared in the following manner. A 25.00 mL sample of the circulating Stretford liquor was taken. This sample was put into a petri dish and dried at 100 C overnight. A known quantity of NaSCN (approximately 0.025 g) was added to this sample and it was then redissolved in 25.0 mL of eluent. A 10.0 mL sample was then

taken and injected into the analytical column through a 0.2 µm pore size filter, sample loop size 10 µL. A second 10.0 mL was taken and to it were added Na_2SO_4 (approximately 0.01 g) and $Na_2S_2O_3$ (approximately 0.01 g). This too was filtered through a 0.2 µm pore size filter and 10 µL was injected onto the analytical column.

Identification of the components was accomplished by comparison with individual component injections. The area of the component peaks was determined by measurement of the height and the width at half peak height.

The following reagents were used in this study:

Anhydrous Na_2HPO_4 (Reagent Grade)	Baker and Adamson (New York, N.Y.)
KH_2PO_4 (monobasic) (Analytical Reagent)	BDH Chemicals Ltd. (Toronto, Ont.)
Cetyltrimethylammonium bromide (Laboratory Reagent)	BDH Chemicals Ltd. (Poole, England)
Anhydrous Na_2SO_4 (Reagent Grade)	J.T. Baker Chemical Co. (Phillipsburg, N.J.)
NaSCN (Reagent Grade)	J.T. Baker Chemical Co. (Phillipsburg, N.J.)
Anhydrous $Na_2S_2O_3$ (Certified)	Fisher Scientific Co. (Fair Lawn, N.J.)

2.2. Ion Exchange Chromatography: Silica Based Technique

This technique allowed for the separation and quantification of the NaSCN, Na_2SO_4 and the $Na_2S_2O_3$ found in the

circulating liquors. The separation was monitored with a conductivity detector. The eluent consisted of a 5 mM solution of KHP dissolved in distilled, deionized water. The pH of the eluent was adjusted to pH 3.55 $\pm$ 0.05 with a saturated solution of phthalic acid (also prepared in distilled deionized water). This solution was then filtered through a cellulose acetate filter (0.8 µm pore size). The solution was degassed using an ultrasonic bath.

A "synthetic" Stretford solution was then prepared containing 3.0 g/L purified ADA, 25.0 g/L Na_2CO_3, 10.0 g/L tri-sodium citrate dihydrate and 1.5 g/L $NaVO_3$. This solution was used in the preparation of the calibration solution.

A spiking solution was prepared containing known concentrations of approximately 6 g/L NaSCN, 6 g/L Na_2SO_4 and 5 g/L $Na_2S_2O_3$ in eluent. Aliquots of this solution (0.50 mL, 2.00 mL and 3.00 mL) were added to exactly 10.00 mL of the synthetic Stretford solution. The pH of this solution was adjusted to pH 3.5 to pH 3.6 using a 1:10 HCl solution. The volume of this solution was further adjusted to exactly 25.0 mL with eluent. The sample was injected onto the Wescan anion exchange column through a 0.2 µm pore size cellulose acetate filter and a 50 µL sample loop. A calibration curve

was plotted with area (by measurement) versus amount of anion injected.

The actual Stretford sample was prepared in a similar manner. A 10.00 mL sample of the circulating liquor was taken and adjusted to pH 3.5 to pH 3.6 using the 1:10 HCl solution. The volume of this solution was then adjusted to exactly 25.0 mL using eluent. This was filtered (0.2 µm pore size cellulose acetate filter) and injected onto the column through a 50 µL sample loop. The concentration of the anions was determined from area calculations.

The eluent was pumped through the Chrompak column at approximately 2.0 mL/min. by a single piston, reciprocating, constant displacement pump. A pulse dampener and silica precolumn were connected between the pump and the injection loop valve. The separation was carried out at room temperature. The guard column consisted of a Whatman Pre-Column Gel (#4191-015). The analytical column, eluent reservoir and conductivity detector were insulated with styrofoam to prevent temperature fluctuations in the conductivity response.

Identification of the components was accomplished by comparison with individual component injections. The area of the component peaks was determined by measurement of the height and the width at half peak height.

The following reagents were used in this study:

Anhydrous Na_2SO_4 (Reagent Grade)	J.T. Baker Chemical Co. (Phillipsburg, N.J.)
NaSCN (Reagent Grade)	J.T. Baker Chemical Co. (Phillipsburg, N.J.)
Anhydrous $Na_2S_2O_3$ (Certified)	Fisher Scientific Co. (Fair Lawn, N.J.)
Potassium Hydrogen Phthalate (Analytical Reagent)	BDH Chemicals Ltd. (Toronto, Ont.)
Phthalic Acid (Reagent Grade)	BDH Chemicals Ltd. (Poole, England)
Na_2CO_3 (Reagent Grade)	J.T. Baker Chemical Co. (Phillipsburg, N.J.)
$NaVO_3$ (Laboratory Grade)	BDH Chemicals Ltd. (Poole, England)
Sodium Citrate, Dihydrate (Reagent Grade)	J.T. Baker Chemical Co. (Phillipsburg, N.J.)
Hydrochloric Acid (Reagent A.C.S.)	Fisher Scientific Co. (Fair Lawn N.J.)

2.3. Ion Exchange Chromatography: Polymer Based Technique

This technique was used to separate and quantify selected components of the circulating Stretford liquor at their natural pH (ie. pH 8 to pH 9). This was attempted using the polymer based Hamilton PRP-X100 anion exchange column which was connected to the same HPLC system described in section 2.2. The only significant changes were that the

tubing leading to and from the analytical column were also insulated with styrofoam. No silica precolumn was used since the separation was at high pH. No guard column was used since the PRP-X100 was still a relatively new product and a compatible guard column packing for use at high pH was not yet available.

To facilitate a separation, the eluent used was 25 mM phenol adjusted to pH 10.15 $\pm$ 0.05 with a 2 M solution of sodium hydroxide. Both of these solutions were prepared in distilled, deionized water. The eluent was filtered through a cellulose acetate filter (pore size 0.8 µm) and degassed in an ultrasonic bath.

A calibration solution was prepared in the eluent and consisted of 25.0 g/L Na_2CO_3, 10.0 g/L tri-sodium citrate, 5 g/L $NaVO_3$, 1.0 g/L $Na_2S_2O_3$, 1.0 g/L Na_2SO_4 and 1.0 g/L NaSCN. Aliquots of this solution (0.50 mL, 2.00 mL and 3.00 mL) were taken and diluted to 10.0 mL with eluent. These samples were injected through cellulose acetate filters (pore size 0.2 µm) and a 50 µL sample loop onto the analytical column .

The above yielded a calibration curve with area plotted against concentration of the anion in question. Area calculations were accomplished through the measurement of the peak height and width at one half of the peak height.

The circulating Stretford liquor was analyzed in a similar manner. A 1.00 mL sample of the Stretford liquor was taken and diluted to 10.0 mL with eluent. This sample was then injected onto the analytical column through a cellulose acetate filter (pore size 0.2 μm) and a 50 μL sample loop. Once again the area was calculated and the concentration of the components were determined from the calibration curve.

The following reagents were used in this study:

Anhydrous Na_2SO_4 (Reagent Grade)	J.T. Baker Chemical Co. (Phillipsburg, N.J.)
NaSCN (Reagent Grade)	J.T. Baker Chemical Co. (Phillipsburg, N.J.)
Anhydrous $Na_2S_2O_3$ (Certified)	Fisher Scientific Co. (Fair Lawn, N.J.)
Na_2CO_3 (Reagent Grade)	J.T. Baker Chemical Co. (Phillipsburg, N.J.)
$NaVO_3$ (Laboratory Grade)	BDH Chemicals Ltd. (Poole, England)
Sodium Citrate, Dihydrate (Reagent Grade)	J.T. Baker Chemical Co. (Phillipsburg, N.J.)
Phenol (Reagent Grade)	Merck and Company, Inc. (Rahway, N.J.)
Sodium Hydroxide (Analytical Grade)	BDH Chemicals Ltd. (Toronto, Ont.)

2.3.1. Linear Dynamic Range Studies

A suite of standard solutions with concentrations of Na_2CO_3 (2.5 g/L), Na_2SO_4 (0.10 g/L), $NaVO_3$ (0.15 g/L),

$Na_2S_2O_3$ (0.10 g/L), Na_3Citrate (1.0 g/L) and NaSCN (0.10 g/L) were prepared. Aliquots of the calibration solution (0.01 mL, 0.02 mL, 0.03 mL, 0.50 mL, 1.00 mL, 2.00 mL, 3.00 mL, 5.00 mL and 6.00 mL) were taken and diluted to 10.0 mL with the eluent. These samples were then analyzed according to the method described in section 2.3.

2.3.2. Eluent Concentration and pH Adjustment

A variety of concentrations of the phenol in aqueous solution was prepared in distilled, deionized water. The concentrations were 25 mM, 30 mM and 35 mM phenol. The pH of these eluents was adjusted to set point values at intervals between pH 9.7 and pH 10.2. A sample consisting of the 1.00 mL calibration solution was prepared and injected according the method of section 2.3. The retention times and resolution were then calculated.

2.3.3. Preparation of Various Eluents

A variety of different eluents were prepared in distilled, deionized water. The eluents are listed in Table 2.3.3.1 including the pH of the eluent used. Individual components of the Stretford liquors were prepared in the concentration used in section 2.3. A solution of NaCl (0.1 g/L) was prepared to determine if a reasonable retention time

could be expected for the Stretford components. All samples injected were prepared in the appropriate eluent.

2.4. Spectrophotometric Study

Individual samples of the anions found in the Stretford liquors were prepared in a 25 mM solution of phenol at pH 10.15. The concentrations of the anions were Na_2CO_3 (25 g/L), Na_2SO_4 (1.2 g/L), $NaVO_3$ (1.5 g/L), $Na_2S_2O_3$ (1.4 g/L), tri-sodium citrate (10 g/L), NaSCN (1.5 g/L) and ADA (3.0 g/L). The concentrations were chosen to be those used in the calibration curve studies and are typical of those in the circulating liquors.

An HP 8451A diode array spectrophotometer was used over the wavelength of 190 nm to 820 nm. The phenol was run with distilled, deionized water as the reference and all other samples were scanned with the phenol as the reference.

TABLE 2.3.3.1
ELUENT CONDITIONS

ELUENT COMPONENT	CONCENTRATION	pH (± 0.05)
Na_2CO_3	3 mM	
$NaHCO_3$	2.4 mM	
Na_2CO_3	1.5 mM	9.80
$NaHCO_3$	1.2 mM	
Na_2CO_3	4.8 mM	10.00
$NaHCO_3$	4.7 mM	
KOH	5.79 mM	11.50
Sulfobenzoic acid	0.5 mM	8.80
Sulfobenzoic acid	0.5 mM	10.00
Sulfobenzoic acid	10 mM	8.30
p-Hydroxybenzoic acid	10 mM	8.55
p-Hydroxybenzoic acid	10 mM	9.50
p-Hydroxybenzoic acid	10 mM	10.00
KHP	5 mM	10.10
p-Hydroxybenzoic acid/phenol	10 mM 20 mM	10.05
Phenol	10 mM	10.13
Phenol	20 mM	9.00
Phenol	20 mM	9.50
Phenol	20 mM	10.00
Phenol	30 mM	9.00
Phenol	30 mM	9.50
Phenol	30 mM	10.00
Phenol	35 mM	9.90

CHAPTER 3

RESULTS AND DISCUSSION

CHAPTER 3

RESULTS AND DISCUSSION

Wet chemical techniques for Stretford liquor analysis are limited in that they are time consuming, there is a variability in sample size depending upon which species is being investigated and the sum of the total anion charges does not equal the sum of the total cation charges found by the analysis. Also, the analytical results do not sum to the total dissolved salts. This results in uncertainty in the analytical results produced. One cannot optimize the conditions in the Stretford process without complete knowledge of these components. HPLC techniques seem to be a viable alternative to wet chemical methods since they may allow for many components of the circulating Stretford liquors to be quantified in the same analysis. HPLC would also reduce the time and cost for each component analysis. As well, it could lead to a detection level lower than currently attainable with wet chemical methods. Thus, the purpose of this project was to gain insight into the various HPLC techniques which could be applicable to the analysis of the circulating Stretford liquors. Such

techniques as ion pair chromatography and ion exchange (both polymer and silica based packings) will be considered.

Virgin Stretford liquors contain vanadium (IV and V) in various anionic species, CO_3^{2-}, HCO_3^-, citrate, OH^- and ADA. The charge balance is primarily maintained by Na^+. Liquors in use also contain by-products of the oxidation of HS^- to elemental sulfur, such as polysulfides, SO_4^{2-} and $S_2O_3^{2-}$, and SCN^- if hydrogen cyanide is present in the feed gas. An ideal method would allow the isolation and quantification of all of these species in one sample. The highest priority is assigned to the quantification of the by-products. An accurate account of their levels allows one to optimize the reaction conditions and to reduce or eliminate the by-product streams. The next important components to be analyzed are vanadium, as V(IV) and V(V), and the ADA since each participates in the redox reactions that oxidize HS^- to elemental sulfur and that regenerate the solution. Lowest in priority is the quantification of the trisodium citrate dihydrate and the Na_2CO_3.

A successful method allows for the quantification of each of the above species. HPLC techniques are the preferred route due to their previous success in anion analysis. The criteria for success are as follows. A Gaussian, or near Gaussian, peak shape, well separated from

others, is attained in a reasonable time for each species. A retention time in excess of 15 to 20 minutes is considered too long since, on a practical level, this would decrease the number of analysis a technician could be capable of accomplishing in one day. Less than 10 minutes would be considered ideal. The next factor to be considered is the reliability of the results. An accuracy and precision better than $\pm$ 10% relative should be the goal since data at these levels are suitable for process analysis, control and optimization. A final criteria to be considered is the resolution between the species eluting. Resolution (R_S) is defined as the following ratio:

$$R_S = \frac{(t_{R2} - t_{R1})*2}{(t_{w1} + t_{w2})} = \frac{(\sqrt{N})\ \ (k')\ \ (\alpha - 1)}{(k' - 1)}$$

where t_{R1} and t_{R2} are the retention times of the two peaks under study, t_{w1} and t_{w2} are the width of the peaks and N is the theoretical number of plates. Ideally a resolution of 1.0 or better is sought since 98% of the two peaks in question would then be resolved. This leads to much better levels of accuracy and precision in the quantitative results obtained. Thus, the criteria of peak shape, retention time, resolution and repeatability must always be kept in mind when developing a method.

The approach taken was to investigate ion pair and then ion exchange methods. The ion pair route was attempted

first since Mistry, under contract to Peabody Holmes Ltd., used this technique to quantify both NaSCN and $NaVO_3$ in the circulating Stretford liquors. Ion exchange methods, especially low pH methods, were then considered since they showed some degree of success in the analysis of Na_2SO_4, $Na_2S_2O_3$ and NaSCN in ground water samples.[37] High pH methods were investigated since the pH of the circulating Stretford liquor is at a pH of approximately 8.0 and it would be advantageous to analyze the liquors without need for pH adjustment. Changes in the pH could lead to changes in the speciation and amounts of the sulfoxy anions of the by-products and in the vanadium catalyst.

3.1. Ion Pair Chromatography

After reviewing the principles of ion pair chromatography, two possible models could be postulated to control the separation process.[38] One model involves the formation of a neutral organic species with the counter-ion. This species was separated by the variation of the concentration of the organic component in the eluent. The typical reactions were as follows with cetrimide (CTMA) as the ion-pairing counter-ion:

$$CTMA^+ + X^- \rightleftharpoons (CTMAX)_{aq}$$

$$(CTMAX)_{aq} \rightleftharpoons (CTMAX)_{org}$$

The basis of a second possible model is essentially that involved in a typical ion exchange process. In this model the counter-ion coats the stationary phase and the anion exchanges with the secondary ion. The buffer solution provides the secondary ion. This is illustrated as follows:

$$-R\text{-}CN(CTMA^+HPO_4^-) + X^- \longrightarrow -R\text{-}CN(CTMA^+X^-) + HPO_4^-$$

$$-R\text{-}CN(CTMA^+X^-) + HPO_4^- \longrightarrow -R\text{-}CN(CTMA^+HPO_4^-) + X^-$$

This second model is the more accepted version for soap chromatography because this approach accounts for the observed role of the secondary ion in the mobile phase.

A reverse phase column (Sil-60-D-10CN) was chosen as the analytical column since Pitts had some success with this column in the analysis of ADA and Na_2SO_4. The detectors

which were used were a UV/Visible detector set at 210 nm and a conductivity detector connected in series. Both detectors were used since species that had no natural chromophores and would not appear on a UV detector could be detected by a change in the conductivity of the solution.

In the design of an experimental approach to method development the experimental variables which could be considered are the counter-ion identity, the counter-ion concentration, the solvent polarity, the buffer concentration, the ionic strength, the pH of the solution and the temperature. Of these possible variables the identity of the counter-ion, its concentration, the pH and the temperature were held constant. Thus, the only variables which remained to be altered were the polarity of the mobile phase and its ionic strength.[39]

The counter-ion is generally responsible for changes in the solvent strength of the solution. This is usually accomplished through changes in its concentration. By increasing the CTMA concentration one could effectively increase the capacity factor, k' of the separation. A change in the number of $-CH_2$ groups in the alkyl chain of the counter-ion would significantly change the selectivity of the separation. This was evident through the considerable difference in the separations achieved when using TBA

rather than CTMA. From previous literature CTMA gave shorter retention times than TBA for disulfonic acids, therefore, it was chosen. These differences have been explained in the section 1.2.

Methanol served as the organic component of the mobile phase and was responsible for changes in the solvent polarity. By increasing the methanol concentration the capacity factor, k' decreased. In ion pair chromatography, the solvent strength played a different role than in most chromatographic separations. The solvent strength was responsible for how well the ions and the ion pairs could be dissolved and stabilized.

One purpose which the secondary ion served was to control the ionic strength of the solution. By increasing the concentration of the $NaHPO_4$ the ionic strength of the mobile phase would increase and the k' would decrease since the ions would have a greater affinity for the mobile phase rather than the stationary phase ie., k' is defined as

$$k' = K_D(V_{stat.}/V_{mob.})$$

and

$$K_D = [conc]_{stat.}/[conc]_{mob.}$$

In most cases, pH would play a crucial role in the separation. The pH was controlled by the ratio of $NaHPO_4$ to K_2PO_4. Since the pKa's of the various anions were all under

pH 4.0 (as seen in the introduction) and the mobile phase pH was approximately at pH 6 to pH 7 the pH of the mobile phase did not play a significant role. Therefore, the mobile phase pH did not aid in the ionization of the species to be separated and was held constant to reduce the background conductivity signal.

The temperature was fixed for convenience sake. In general, though a higher temperature would yield a lower retention time since temperature would increase the selectivity, α.

In the experimental design, a standard addition approach was taken. To accomplish this, the sample was injected onto the analytical column. A second aliquot of sample was spiked with known quantities of the species in question and injected. This allowed one to determine the initial concentrations of the species.

By using a standard addition approach the possibility of interference (ie. peak overlap) caused by the presence of an internal standard was eliminated. The concentration of the species was determined by relating the resulting change in area of the peak to the concentration of the spike. The area of the peak was determined through measurement of the peak height and the width at half the peak height (See Appendix 2 for definition). This method

was successful in the separation and determination of the Na_2S, Na_2SO_4, NaSCN and $Na_2S_2O_3$.

The detection system which was used was a UV/Visible spectrophotometer adjusted to 210 nm in series with a conductivity detector. The spectrophotometric detection allowed for the detection of the chromophores associated with Na_2S, NaSCN and $Na_2S_2O_3$. Since Na_2SO_4 did not have any chromophores the conductivity detection system allowed for the detection of this species. This detector also allowed one to detect the $NaHCO_3$ which was found in the mobile phase. The conductivity detector was placed prior to the UV/Visible detector since the dead volume associated with this detector was smaller than the dead volume associated with the UV/Visible detector. A lag time would occur and this would result in band broadening since the mobile phase and samples could remix in this period of time had the detectors been placed the opposite way in series.

In the preliminary experiments, the buffer solution was prepared at a concentration of 0.1 M Na_2HPO_4 and 0.1 M KH_2PO_4. This gave a high ionic strength for the mobile phase solution and also had an adverse effect on the conductivity detection system, that is a large background signal. Various ratios of buffer solution to methanol were attempted ranging from 65% buffer to 55% buffer. At high

ratios of buffer to methanol the analyte or sample anions eluted slowly and gave asymmetric peaks with extensive tailing whereas with a lower ratio the sample anions eluted with the solvent front. The aqueous stock solution of the mobile phase was lowered in concentration to 0.004 M Na_2HPO_4 and 0.016 M KH_2PO_4. With a ratio of 54% methanol to 46% buffer individual samples of the species were prepared and injected. A retention time of 6 minutes was obtained for NaSCN, 8 minutes for $Na_2S_2O_3$ and 5 minutes for Na_2SO_4 and all of the peak shapes were Gaussian. When a mixture was prepared there was a loss of resolution. This could not be explained. The mobile phase was adjusted to 47.5% methanol and 52.5% buffer to improve the resolution.

Since a water peak showed interference in the range where the species eluted the actual circulating liquor samples were taken to dryness and redissolved in the eluent prior to injection. These raw solutions were not diluted prior to injection. Freeze drying was also attempted, however, the apparatus was not successful in removing all of the water and this technique was not further investigated. A more practical solution would have been to dilute the sample with a concentrated stock of eluent. This would have significantly reduced the interference due to water.

Thus, the final approach which was used to analyze for the species was a mobile phase at 47.5% methanol and 52.5% for the aqueous portion and the sample was oven dried and then redissolved in the mobile phase.

Two different methods could be used in the quantification of the species present, namely standard addition or calibration curve. The standard addition approach was used since any matrix effects would be reduced

Two approaches were taken to select the internal standard. The first was to use the species which would be least common in the circulating liquors, that being the NaSCN which was only present if hydrogen cyanide were present in the feed gas. The second approach was to use a species present which would not be a by-product. This pointed to the use of the $NaHCO_3$ peak as the internal standard. Since the $NaHCO_3$ was seen only by the conductivity detection system it was used as the internal standard for the Na_2SO_4 and the $Na_2S_2O_3$. The NaSCN was detected in both systems and was used as the internal standard for the UV/Visible detection system. It allowed for the determination of the Na_2S and the $Na_2S_2O_3$.

Comparison of the $Na_2S_2O_3$ concentration calculated from the $NaHCO_3$ and NaSCN internal standards showed a difference of about 25%. This difference is due to error

resulting from the use of $NaHCO_3$ as an internal standard. One did not have control over the concentration of the carbonate/bicarbonate buffer solution due to dissolved CO_2 in the solution. Since the liquors were taken to dryness and redissolved in the mobile phase further loss of control of concentration resulted. Thus, carbonate/bicarbonate was a poor choice as an internal standard and another species should have been used as the internal standard in conductivity detection.

The resolution between $Na_2S_2O_3$ and $NaHCO_3$ in the conductivity detection system and between NaSCN and $Na_2S_2O_3$ in both conductivity and UV/Visible detection systems presented a problem since they were poorly resolved. Before spiking with aliquots of Na_2S, Na_2SO_4 and $Na_2S_2O_3$ the resolution between the species was adequate but after spiking it decreased significantly. A decrease in the polarity of the mobile phase would lead to larger k' values, however, the peaks broadened and the retention times increased to the point that the areas could not be accurately determined and the analysis time was significantly increased.

A compromise was made between resolution and analysis time favoring a shorter analysis time. Typical chromatograms are provided in Figure 3.1.1 and Figure

3.1.2. These figures show a typical circulating Stretford liquor sample AHT 020 before and after spiking (ie. APH150-062685 and APH152062685 respectively) with known aliquots of the anions involved. Retention times and resolutions for the species present are listed in Table 3.1.1. Note the significant decrease in the resolution between the NaSCN and the $Na_2S_2O_3$ after spiking. This effect could not be explained. Quantitative results for the species are listed in Table 3.1.2 for a typical Stretford solution (ie. AHT 020). An attempt to use this sample as a quality control standard was unsuccessful because it showed a wide range in the 95% confidence interval; thus, quantitative control was not evident.

Ion pair chromatography is recommended for the separation of species which are very polar and that have multiple ionization states or are strongly basic species.[40] Since the components of the circulating Stretford liquors met most of these requirements it was considered a reasonable route to follow. Furthermore, previous work had been done on very ionic and polar compounds such as the amino or hydroxy sulfonates of naphthalene with soap chromatography. Standard LC methods could not separate these species, however, soap chromatography (using CTMA as the counter-ion)

resulted in separations with fairly good resolution and band shapes.

This route to the analysis of Stretford liquors had a limited scope since NaSCN could not be determined but had to be used as an internal standard. Furthermore, resolution was inadequate at best. Change in pH had no effect on the separation and a change in the counter-ion concentration also had no effect since the species were all fully ionized. A change in the secondary ion might provide for better resolution, however, it would lead to a larger background conductivity which would limit the usefulness of this detector. Thus, of all the parameters available to change only the solvent polarity could be altered to allow for detection and separation. This was altered and did not allow for adequate resolution, therefore, a different route was attempted.

3.2. Ion Exchange Chromatography

Ion exchange techniques are well established and have been used in HPLC systems for many years. Their most common use has been in the analysis of organic acids and bases. The technique could also be applied to inorganic anion analysis. Since the main species present in circulating Stretford liquors are the anions of inorganic salt species this seems to be a reasonable route to investigate. Thus, the technique of ion exchange chromatography was applied to the analysis of the by-products (Na_2SO_4, $Na_2S_2O_3$ and NaSCN) as well as to the components of the virgin Stretford liquors ($NaVO_3$, ADA, tri-sodium citrate dihydrate and carbonate/bicarbonate).

For any ion exchange method there are basic variables to consider which will elicit an observable response in the separation. They are the identity of the column, the nature of the species present in solution and their concentrations, the pKa values and ionic strength of the eluent anion, the temperature of the analysis and the kind of eluent anion used from the perspective of how many protons can be hydrolyzed.41

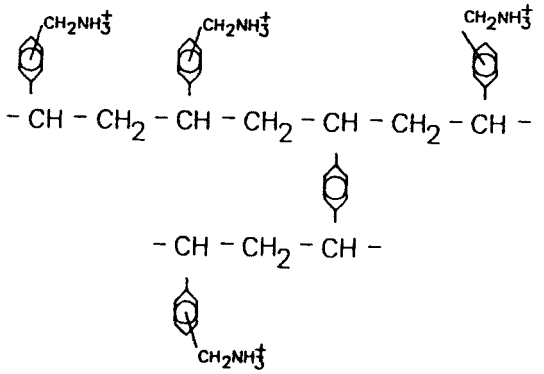
In this study, the temperature was fixed at room temperature for convenience. This reduced the number

of variables to deal with. Each of the variables will be discussed in some detail.

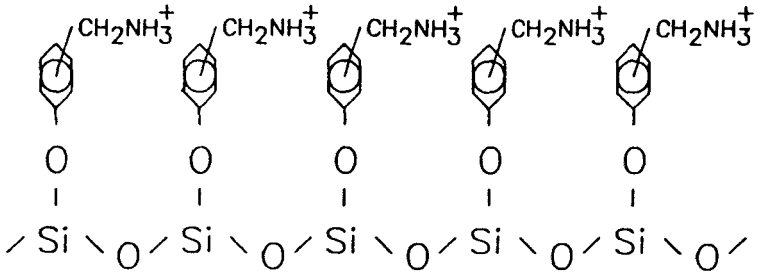
When approaching a separation, five factors are generally encountered. They are the kind of column used, the eluent used, the detector used, the experimental design and the methods of calculation. Control of the variables mentioned above contributes significantly to the success or failure of a method.

There are two different types of columns to choose from when investigating single column ion exchange chromatography; namely silica and polymer based columns.[42] Their differences rest mainly in the working pH ranges. Silica based columns are well established, are more commonly used, and have a lower working pH range; ie., pH 2.5 to 5.5. The polymer based columns are relatively new and it is claimed that their working range extends from pH 1.0 to pH 13.0.

Structurally speaking, polymer based stationary phases in ion exchange columns have ionic functional groups (such as NH_3^+) attached to a styrene divinylbenzene backbone as in the following figure:



Silica based stationary phases have the functional groups grafted onto a silica backbone through the use of organic connecting groups. This is illustrated in the following diagram:



Regardless of which stationary phase is being used, the separation model involved is the same. Two equilibria should be considered, the first is a distribution of the species involved between the stationary phase and the mobile phase or solution followed by the reaction with the ionic sites of the stationary phase.[43] The controlling factor of the exchange model is not the reaction between the species and the ionic sites of the stationary phase, rather, it is the partitioning between the aqueous and the organic (ie. stationary) phases. Thus, by lowering the pH of the mobile phase or solution the species investigated would be retained for a longer period of time on the organic (ie. stationary) phase. This would result in a longer

retention time. With a high pH, the eluent anion would be ionized to a greater extent and this would lead to a lower retention time for the species in question. This is illustrated in the following:

$$HX_{soln} \rightleftharpoons HX_{stat}$$

$$HX_{stat} \rightleftharpoons H^+ + X^-$$

$$RY + X^- \rightleftharpoons RX + Y^-$$

$$HY \rightleftharpoons H^+ + Y^-$$

$$HY_{soln} \rightleftharpoons HY_{stat}$$

where HX_{soln}: species in aqueous (mobile) phase

HX_{stat}: species in organic (stationary) phase

HY_{soln}: eluent anion species in aqueous (mobile) phase

HY_{stat}: eluent anion species in organic (stationary) phase

When choosing an eluent anion, one must consider many factors already encountered, namely the pH and ionic strength, the temperature, the concentration of the eluent anion, the conductivity and the organic sample anions in question.

The pH dictates the extent of ionization of the eluent anion. A higher pH will allow for the complete ionization of any eluent chosen.

The eluent anion concentration affected the capacity factor, k'. A higher eluent anion concentration would

result in a greater competition for the ion exchange sites of the stationary phase. This would cause any sample anions to be eluted to a greater extent and the selectivity, α, of the separation would decrease. Eluent anion concentration also played a significant role when a conductivity detection system was used. A high eluent anion concentration would also increase the conductivity of the mobile phase and affect the capability of the detector to suppress the background signal. The type of eluent anion used also affects the conductivity signal. Large organic molecules, such as phenol, have much lower conductivities than smaller molecules, such as KOH, mainly due to differences in mobility. Therefore, higher concentrations of these larger molecules can be tolerated before it is no longer possible to electronically suppress the background signal.

The pKa of the eluent anion must also be considered because it controls the working pH range. For instance, phthalic acid has two pKa values (2.94 and 5.43) and can function over a working pH range of 1.94 to 6.43.

Two kinds of detectors are commonly used in single column electronically suppressed ion chromatography; namely UV/Visible and conductivity detectors. The detector more commonly used is the conductivity detector. It is a universal detector and responds to any change in conductiv-

ity. Many detectors are now capable of electronically suppressing the mobile phase (ie. background) signal and are, therefore, making these systems cheaper to use than the chemically suppressed two column ion exchange systems. UV/Visible detectors have been used in some innovative manners in ion chromatography. A literature example is the use of this detector with an eluent anion with a large Λ_{max} (where Λ_{max} is the absorption maximum). Thus, when the sample anion elutes, its Λ_{max} is substantially less than that of the eluent anion and the signal is detected as a negative peak on the chromatogram.

The experimental design can follow two approaches. They are standard addition and calibration curve techniques. Each method has been attempted to see if there is a correlation between the methods. The calibration curve technique required the determination of linear dynamic ranges for each of the species eluted and then the subsequent regression analysis. Once again, as with ion pair chromatography, the areas of the peaks were calculated by the product of the peak heights and the width of the peaks at half height. The data were correlated with the concentration of the sample in the calibration curve or with the spike concentration in the standard addition method.

3.2.1 Silica Based Technique

Since a silica based anion exchange column was used in this separation scheme the mobile phase pH had to be restricted to the range of pH 2 to pH 5.5. By working inside of this window, one ensured that the backbone to this column did not degrade as in the following reaction:

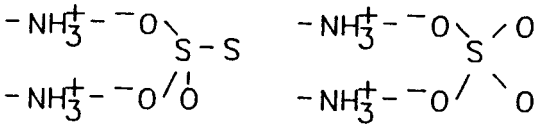
$$SiOH + OH^- \text{ ---> } SiO^- + H_2O$$

The most common eluent anion used for the separation of aqueous sulfur anions had been potassium hydrogen phthalate (KHP). This eluent anion was used because it has a low conductivity, therefore, if a conductivity detector is used the background conductivity could be easily suppressed. Another advantage is that this eluent anion could work over a relatively wide pH range with pKa values of 2.94 and 5.43.

Various concentrations ranging from 4 mM to 8 mM were considered when HP^- was used as the eluent anion. The three by-product species of NaSCN, Na_2SO_4 and $Na_2S_2O_3$ were separated using this technique and eluted as Gaussian-shaped peaks. The best resolution between the NaSCN and the $Na_2S_2O_3$ was attained at 5 mM KHP and at pH 3.50. It was then attempted to find an internal standard. From the species selected, (ClO_4^-, $Cr_2O_7^{2-}$, Cl^-, NO_3^-), all either eluted just past the solvent front or with the species of

the circulating liquors. Thus, the method of standard addition without an internal standard was used and compared to a calibration curve method.

The sample anions simply eluted as the singly charged species followed by the doubly charge species. The doubly charged species would bind to the stationary phase with two sites, in analogy with bidentate ligands and had a stronger affinity for the stationary phase and longer retention times.[44] This is illustrated in the following diagram:



It should be noted that coulombic attractions rather than covalent bonds are implied.

The linear dynamic range was determined for each of the by-product species. This allowed one to determine the working range for the quantitative analysis. The working range for actual column loading was up to 30 µg for the $Na_2S_2O_3$, up to 60 µg for the Na_2SO_4 and in excess of 150 µg for the NaSCN. The linear dynamic ranges are illustrated in

Figures 3.2.1.1 through Figures 3.2.1.3. Analysis of variance (ANOVA) plots and the least squares lines are listed in Table 3.2.1.1 through Table 3.2.1.3. The analysis of variance plots tested the linear model to determine if it were appropriate or if the data points were just random points.[45] The model $y=\beta_0 + \beta_1 x$ was tested to see if β_1 was significant.

The retention times for the species eluted were approximately 5.0 minutes for $NaHCO_3$, 6.8 minutes for NaSCN, 7.3 minutes for Na_2SO_4 and 8.9 minutes for $Na_2S_2O_3$. The resolution between the respective peaks was 2.39 between the NaSCN and the Na_2SO_4 and 2.03 between the Na_2SO_4 and the $Na_2S_2O_3$ at a pH of 3.5 and an eluent anion concentration of 5 mM KHP.

A response surface investigation between resolution and concentration of KHP showed a trend to increased resolution at lower eluent anion concentration. This was a favorable result since a lower eluent anion concentration would result in a lower background conductivity with the conductivity detection system. These data are available in Table 3.2.1.4.

A response surface investigation of the effect of pH on resolution gave a similar trend. Higher pH values resulted in lower retention times and also improved resolu-

tion. The use of higher pH presented a problem since the silica based ion exchange packing would have a substantially shorter lifetime due to degradation. When a lower pH was used asymmetric peak shapes resulted. Asymmetric peak shapes consequently led to errors in the determination of the peak area. This was particularly evident for the $Na_2S_2O_3$ peak at pH 3.8 and at an eluent anion concentration of 6 mM. Thus, a relatively low pH with a low concentration of eluent anion (ie. less than 6 mM) was the best choice for the mobile phase. These data are available in Table 3.2.1.5. The response surface investigations are illustrated in Figure 3.2.1.4 and a typical chromatogram is shown in Figure 3.2.1.5.

After a period of two months of analysis the ion exchange column did show signs of degradation. A peak, thought to be associated with the tri-sodium citrate appeared beneath the NaSCN and Na_2SO_4 peaks. This peak was broad enough that one could simply regard it as a drifting baseline (typical of a gradient analysis) and still obtain quantitative results.

A statistical analysis for the quantitative results of the by-product analysis is given in Table 3.2.1.6. The relative error associated with the method is $\pm$ 0.3% for NaSCN (concentration 0.1763 mg/mL), $\pm$ 5.9% for Na_2SO_4

(concentration 0.1799 mg/mL) and ± 9.1% for $Na_2S_2O_3$ (concentration 0.1467 mg/mL).

The statistical analysis results are encouraging since the relative error is less than ± 10% for the three by-products and the analysis is completed in under 15 minutes. This could not be accomplished using wet chemical methods. Since the solution is buffered to pH 3.5 from pH 8.5 prior to analysis this could be considered a drawback. The by-products could easily change forms between various sulfur species or a pH dependent equilibrium between the Na_2SO_4 and the $Na_2S_2O_3$ could exist. A typical reaction is as follows:

$$S_2O_3^{2-} + H^+ \text{ ---> } HSO_3^- + S \text{ (reversible)}$$

Another drawback to this technique is the fact that dilution factors must be considered. One example of this could be the Na_2SO_4. Since it could be present up to the 92,000 ppm level in circulating Stretford liquors, one must impart a 1/500 dilution in order to obtain the 200 ppm range which one is able to work in for this species. However, one is encouraged by the control over the precision of the method and over the accuracy of the results.

The method is partially successful since the by-products can be determined. However, it does have its drawbacks since none of the components of the virgin

Stretford liquors can be determined. Furthermore, the change of the pH of the solution may cause interconversion of the sulfoxy anions. Therefore, an ideal method would be one in which the pH of the eluent was identical to that of the circulating Stretford liquors. This would ensure that the by-products would not interconvert between any other sulfoxy anions. In order to develop such a method conventional silica based ion exchange columns could not be used. Rather, the newly available polymer based HPLC ion exchange columns should be investigated.

3.2.2. Polymer Based Technique

Since a polymer based ion exchange packing has a pH range of 1 to 13 a greater variety of eluents could be used. Working at higher pH and with many different eluents provides the possibility of resolving the V(IV) and V(V), the tri-sodium citrate, carbonate/bicarbonate and the ADA along with the by-products of Na_2SO_4, $Na_2S_2O_3$ and NaSCN.

A review of previous literature suggested many different eluent anions could be used at higher pH levels. The reason that higher pH conditions were chosen was to prevent the by-products from converting into different sulfoxy anions.[46]

The eluent anions which were considered were carbonate/bicarbonate, KOH, substituted benzoic acids, KHP and phenol. Carbonate/bicarbonate and KOH were investigated since some success had been seen with these eluent anions in suppressed systems. It was thought that at high pH and with low concentrations of these eluent anions separations could be achieved.

Carbonate/bicarbonate was a successful eluent anion for the separation of many species in suppressed systems.[23,24] Since carbonate/bicarbonate was the medium in which the Stretford chemistry took place, by using it as an eluent anion, it would not appear in the chromatograms

(since the signal would be suppressed). One possible matrix factor would then be eliminated.

The concentration of this eluent anion was kept low in order to allow the signal from the species eluted to be detected beyond the background signal of the eluent anion. The concentration of the eluent anion ranged from 1.5 mM $NaHCO_3$/1.2 mM Na_2CO_3 at pH 9.8 to 4.8 mM $NaHCO_3$/4.7 mM Na_2CO_3 at pH 10.0.

Carbonate/bicarbonate as an eluent anion showed limited success. The $NaVO_3$ appeared as at least two to three peaks (both positive and negative) with retention times varying from 3.35 minutes to 24 minutes. It seemed reasonable that various oxyanions had been formed and retained for different periods of time. Typical species in this pH range would be $H_nVO_4^{(3-n)-}$, $H_nV_2O_7^{(4-n)-}$, VO_3^- and $(VO_3)_n^{n-}$ where n=3, 4 or 6.[2] The ADA showed some promise since a single peak appeared with a retention time less than 10 minutes. The tri-sodium citrate appeared as both positive and negative peaks with retention times varying from 3.1 minutes to broad peaks up to 25 minutes. The carbonate/bicarbonate was, therefore, not a suitable eluent anion since it would be impossible to quantify sample anions which eluted as two or three peaks, the retention times were very long for the tri-sodium citrate and peak shapes did not

approach Gaussian shapes. These data are tabulated in Table 3.2.2.1.

Okada and Kuwamoto presented interesting work with KOH as an eluent anion for organic anion determination.[32] They showed that it was a successful eluent anion for the separation of large organic anions. At a low enough concentration (5.79 mM, pH 11.5) the background conductivity would not be significant and the sample anions should elute. When using this eluent anion the $NaVO_3$ eluted as two peaks the longest of which was retained for 59 minutes. The ADA eluted between 15 and 30 minutes and the tri-sodium citrate eluted between 46 and 60 minutes. All three species tested eluted as very broad peaks, thus, the eluent anion concentration was not high enough to cause the exchange of the eluent anion with the sample anions which were bound to the stationary phase. The concentration could not be increased since the electronic suppression would not be able to suppress the background conductivity.

Substituted benzoic acids, as eluent anions, had been used successfully in the separation of species such as citric acid. These were used since they had low conductivities yet the functional groups allowed for interactions with the anions and the stationary phases. The success rate

of these eluent anions on the Stretford anions was determined.

For most ion exchange systems Cl^- is a very weakly retained anion. Cl^- is a relatively small anion and does not interact very strongly with stationary phases. By using NaCl as an indicator; one can infer the retention times of the strongly retained Stretford anions.

The first of the substituted benzoic acid species to be investigated was sulfobenzoic acid. Sulfobenzoic acid was chosen as a possible eluent anion since it had a sulfonic acid group which should cause it to behave in a similar manner to ADA as well as the carboxylic acid group which should cause it to behave similar to the tri-sodium citrate. Only one pKa was available for this eluent anion at pKa 3.65. A concentration of 0.5 mM and pH 8.8 was chosen as the first eluent anion conditions since a low concentration would allow for greater detector sensitivity and this pH was in the pH range of the circulating liquors. The NaCl peak did not elute until well after 15 minutes. The pH was adjusted to pH 10.0 and the NaCl peak exhibited extensive fronting with a retention time of 9.8 minutes. The concentration had to be increased to allow for displacement of the anion from the stationary phase. At a concentration of 10 mM and pH 8.3 the NaCl peak eluted after 1.8 minutes. Individual samples of $NaVO_3$, ADA and tri-sodium

citrate were then prepared in the eluent. After injecting individual samples of $NaVO_3$, ADA and tri-sodium citrate it became evident that this eluent anion was not suitable. Following a wait of 15 and 25 minutes after the injection of the $NaVO_3$ and the ADA respectively not a single peak had eluted.

The tri-sodium citrate did, however, elute after 4.2 minutes. The size of the sulfobenzoic acid could be responsible for the fact that the $NaVO_3$ and the ADA did not elute. Since sulfobenzoic acid was a large molecule with two functional groups it may not have be able to effectively approach the stationary phase and displace the Stretford anions. A more reasonable explanation would be that the ADA and the $NaVO_3$ were more effective in binding to the $-NH_3^+$ sites of the stationary phase. Furthermore, the bulk of the additional functional group on the sulfobenzoic acid as well as the pH and concentration of the eluent anion at which the exchange was attempted could have contributed to the failure of the sulfobenzoic acid as an effective eluent anion.

By replacing the sulfonic acid group with an hydroxyl group (p-hydroxybenzoic acid) the steric effect of the eluent anion should be decreased and the ADA, $NaVO_3$ and the tri-sodium citrate should readily elute. NaCl was again used as a reference peak. The eluent anion was prepared at

a concentration of 10 mM and at a pH of 8.55. The pKa values of p-hydroxybenzoic acid fell at 4.57 and 9.46. Thus at pH 8.55 the p-hydroxybenzoic acid would be singly and partially doubly ionized. When NaCl was injected it eluted after 1.5 minutes. The $NaVO_3$ eluted as two peaks, the first peak eluted between 5 and 9.3 minutes and was very broad. The second appeared as a negative peak at 12.2 minutes. Thus, two oxyanions of vanadium were present. The ADA eluted as a single peak though with a retention time of 10.8 minutes and as a negative peak. Therefore, its conductivity was less than that of the eluent anion. The tri-sodium citrate eluted as three different peaks at 10.1 minutes, a negative peak at 11.2 minutes and a long tailing peak between 16 and 24 minutes. When the ADA sample was spiked with Na_2CO_3 a single peak was seen after 10.8 minutes, thus, what had been initially been thought to be an ADA peak was actually the peak due to the dissolved CO_2 in the solution.

Potassium hydrogen phthalate (KHP) was successful in the separation of the by-product anions at pH 3.5. It was considered a potential eluent anion since at higher pH it might prove successful to separate both the by-product anions as well as the other components of the circulating liquors. Thus, a complete analysis might be possible. The pKa values of phthalic acid were 2.93 and 5.43, therefore,

at a higher pH it would exist as the fully ionized species. A 5 mM solution at pH 10.1 was prepared. The NaCl eluted after 1.9 minutes. However, the KHP was not effective at displacing the sample anions from the stationary phase. The $NaVO_3$ eluted as a broad peak at 3.8 minutes and the ADA as a hump over the range of 6 to 30 minutes. The tri-sodium citrate did have a reasonable retention time at 5.7 minutes and did appear somewhat Gaussian in shape.

Since two carboxylic acid groups on the phthalic acid were effective in causing the $NaVO_3$, ADA and the tri-sodium citrate to elute as single peaks, three carboxylic acid groups may cause them to elute in a reasonable time and with Gaussian peak shapes. Trimesic acid (1,3,5-benzene tri-carboxylic acid) was used. The pKa values of trimesic acid were 2.13, 3.89 and 4.70 and it would be ionized at a higher pH. At a concentration of 0.52 mM and pH 9.33 the NaCl eluted as two peaks, the first was negative and had a retention time of 1.6 minutes whereas the second was positive and had a retention time of 4 minutes. The $NaVO_3$ appeared as a negative hump at 6.9 minutes and the tri-sodium citrate eluted as a wide positive peak between 17 and 25 minutes. ADA, once again, did not elute after 30 minutes. Since the retention times became longer by changing to a tri-substituted eluent the steric effects

played a far greater role in the separation than previously thought. The retention times for these substituted benzene species at different concentrations and pH are given in Table 3.2.2.2.

By decreasing the functional groups on the benzene to only a hydroxyl group it was thought that the steric effects between the eluent anion and the stationary phase would be significantly decreased. Therefore, phenol was chosen as an eluent anion. The pKa of phenol is 9.99 and at a pH greater than pH 10 it would be nearly fully ionized. A 10 mM solution at pH 10.13 was prepared. The NaCl peak eluted after 2.8 minutes. After injecting with the $NaVO_3$ a single Gaussian peak was seen after 7.7 minutes. The tri-sodium citrate also eluted as a single peak though with tailing in the region of 19 to 25 minutes. Once again the ADA did not elute. Since the species of the circulating liquors appeared Gaussian or approached Gaussian shapes, with the exception of ADA, it was thought to proceed and develop a method without ADA present. ADA has two sulfonic acid groups and it is proposed that high coulombic interactions exist between the sulfonic acid groups and the ion exchange sites. If this were the case, these high coulombic interactions would render ion exchange chromatography

ineffective as a possible means of separating ADA from other components of the circulating Stretford liquors.

In order to decrease the tailing on the tri-sodium citrate peak, the pH and the concentration of the phenol were altered. A solution at 25 mM and pH 10.1 to 10.2 gave the best peak shape. The effect of pH and concentration on the retention times of the $NaVO_3$ and the tri-sodium citrate are given in Table 3.2.2.3. When the phenol was adjusted to pH 9.9 and 35 mM a sample with all the components of the circulating Stretford liquors gave retention times of 2.0 minutes for the Na_2CO_3, 3.6 minutes for the $NaVO_3$, 4.9 minutes for the tri-sodium citrate, 2.75 minutes for the $Na_2S_2O_3$, 2.65 minutes for the Na_2SO_4 and 6.9 minutes for the NaSCN. Gaussian peak shapes were evident for all of these species.

Since ADA would not elute off of the column the following calibration solutions were prepared without the ADA to extend the lifetime of the analytical column. A response study of the effect of concentration and eluent anion pH on resolution was undertaken. The results are listed in Tables 3.2.2.4 and 3.2.2.5. Optimum conditions were obtained at a lower eluent anion concentration and at a higher pH. The best conditions were at a phenol concentration of 25 mM and a pH of 10.22. When routine

analysis was undertaken, the eluent anion concentration was lowered to 20 mM in order to reduce the background conductivity of the eluent anion. This had little effect on the resolution between the species eluting, however, it did help increase the sensitivity of the detector.

Preliminary work indicated that the phenol was the most appropriate eluent anion. It had a relatively low conductivity at the concentration used. With phenol one was able to detect the by-products and the components of the virgin liquors (with the exception of ADA). The optimum conditions for the separation were determined through a response surface investigation. The best conditions were obtained at a concentration of 20 mM phenol and a pH of 10.15.

Two different approaches were used in the quantification of the circulating Stretford liquor components. They were a calibration curve method and a standard addition method. Samples were again prepared without ADA present in order to extend the lifetime of the ion exchange column. In order to use a calibration curve, the linear dynamic range for each species had to be determined. A spiking solution was prepared which contained Na_2CO_3 (25.02 g/L), Na_2SO_4 (1.008 g/L), $NaVO_3$ (1.492 g/L), $Na_2S_2O_3$ (1.012 g/L), Na_3Citrate (10.028 g/L) and NaSCN (0.964 g/L). Aliquots

ranging from 0.01 mL to 6.00 mL were taken and diluted to 10.0 mL with eluent. 10 µL of each of these samples were injected, the areas were determined and plotted against the amount of sample injected. Resolutions were determined between the species eluted. A typical chromatogram for the calibration solution is given in Figure 3.2.2.1 and for a synthetic Stretford solution (ie. without ADA or the by-products) is given in Figure 3.2.2.2. The resolution relative to aliquot injected is given in Table 3.2.2.6. The linear dynamic range data for each anion eluted is listed in Table 3.2.2.7 to Table 3.2.2.12. An analysis of variance (ANOVA) for each particular data set testing the model $y=\beta_0 + \beta_1 x$ was also performed. The least squares plots are listed in Figure 3.2.2.3 through Figure 3.2.2.8. Since β_0 and β_1 are significant for all of the data sets the straight line model was applicable for each anion eluted.

The working range for the species eluted was 12 to 250 µg for Na_2CO_3, 2 to 20 µg for $Na2SO_4$, 3 to 30 µg for $NaVO_3$, 2.5 to 25 µg for $Na_2S_2O_3$, 25 to 200 µg for Na_3Citrate and 2 to 30 µg for NaSCN. The accuracy of the method is ± 9.0% for Na_2CO_3, ± 3.1% for $Na2SO_4$, ± 1.5% for $NaVO_3$, ± 2.8% for $Na_2S_2O_3$, ± 18.0% for Na_3Citrate and ± 7.7% for NaSCN.

Dilution factors present a problem with the analysis of the circulating Stretford liquors. Vanadium is usually present in the 60 to 600 µg range whereas the linear range is 3 to 30 µg. Thus, a tenfold dilution is necessary. This tenfold dilution is also necessary for citrate (500 to 4,000 µg) with a 25 to 200 µg linear range and for CO_3^{2-}/HCO_3^- (240 to 5,000 µg) with a 12 to 250 µg linear range. However, for SO_4^{2-} the linear range is only 2 to 20 µg whereas it could be present in the 40 to 4,000 µg range. This would need a 400 fold dilution. Thus, two analysis are required to determine these species rather than one analysis. The SCN^- and the $S_2O_3^{2-}$ concentrations vary depending upon the feed streams and, therefore, could be present in variable quantities.

A comparison of the reliability of the standard addition method relative to the calibration curve method had been undertaken and the calibration curve method showed a much smaller percentage difference from the actual result. The data for the calibration curve results is listed in Tables 3.2.2.13 and 3.2.2.14. The data for the standard addition method is listed in Tables 3.2.2.15 and 3.2.2.16. Thus, calibration curve techniques proved to be the recommended route of analysis.

Since ADA did not appear with the conductivity detection system, there was a possibility that the ADA conductivity was similar to that of the eluent anion and, thus, no signal was measured. A solution of ADA was prepared in the eluent at a concentration level similar to that seen in the circulating Stretford liquors. This was injected directly into the detectors (both conductivity and UV/Visible). Signals were observed, one at each detector. This clearly showed that the detectors were sensitive toward the presence of ADA. This was further confirmed by UV/Visible scans of phenol, ADA and the other components of the circulating liquors were measured. The ADA and the other components were measured relative to phenol in the concentrations used in the quantitative study. The phenol concentration was 20 mM at a pH of 10.15. ADA had a Λ_{max} at 342 nm under these conditions, whereas none of the other species had such a Λ_{max}. These UV/Visible scans are given in Figure 3.2.2.9 through Figure 3.2.2.16. The UV/Visible detector was installed in series following the conductivity detector and adjusted to 342 nm. A neat sample of ADA prepared in eluent was injected at the same concentration as above. After waiting for a period of 30 minutes no peaks were visible through either the conductivity or the UV/Visible plots.

This polymer based anion exchange method is the most reasonable route to separate and quantify six of the seven components of the circulating Stretford liquors (those being Na_2SO_4, $Na_2S_2O_3$, NaSCN, $NaCO_3$, $NaVO_3$ and tri-sodium citrate dihydrate). The resolution is greater than 1.00 for all cases, thus the peaks are 98% resolved among the species eluted, the analysis is complete in under 15 minutes, the peaks are Gaussian in shape and the results for the by-products and the $NaVO_3$ are quantitative with an accuracy better than $\pm$ 10%.

TABLE 3.1.1

RESOLUTION BETWEEN SPECIES
BY ION PAIR CHROMATOGRAPHY

RUN #	DETECTOR	SPECIES	t_R(min) ($\pm$0.05)	R_s ($\pm$0.05)
APH150062685	UV	Na_2S	4.1	
				7.70
		NaSCN	11.8	
				0.84
		$Na_2S_2O_3$	13.1	
	Conductivity	Na_2SO_4	10.2	
				1.28
		NaSCN	11.8	
				0.87
		$Na_2S_2O_3$	13.1	
				0.60
		$NaHCO_3$	14.7	
APH152062685	UV	Na_2S	4.1	
				6.57
		NaSCN	11.6	
				0.40
		$Na_2S_2O_3$	12.4	
	Conductivity	Na_2SO_4	9.8	
				1.33
		NaSCN	11.6	
				0.42
		$Na_2S_2O_3$	12.4	
				0.79
		$NaHCO_3$	14.8	

TABLE 3.1.2

STANDARD ADDITION RESULTS: ION PAIR CHROMATOGRAPHY
June 5, 1986 to August 13, 1986

Na_2S (g/L) (wrt NaSCN)	Na_2SO_4 (g/L) (wrt $NaHCO_3$)	$Na_2S_2O_3$ (g/L) (wrt NaSCN)	$Na_2S_2O_3$ (g/L) (wrt$NaHCO_3$)
0.00173	0.0003480	0.0003890	0.0008078
0.00653	0.0007300	0.0003990	0.0005710
0.00699	0.0009369	0.0003300	0.0007614
*0.00471	0.0010220	0.0002770	0.0007992
*0.01359	0.0009156	0.0006109	0.0001250
*0.01380	0.0009916	0.0003478	0.0002387
----------	0.0004890	0.0007389	*0.0017539
AVG: 0.00508	0.0002209	0.0003129	*0.0000234
s: 0.00240	0.0007394	0.0002815	----------
C.I.-0.0008	0.0009987	0.0003606	AVG: 0.0005505
to: 0.0110	0.0007313	0.0003282	s : 0.00030
	0.0009371	0.0004616	C.I. 0.0003
	*0.0020000	0.0005046	to: 0.0008
	---------	---------	
	AVG: 0.0007550	AVG: 0.0004109	
	s : 0.0003	s: 0.0001	
	C.I. 0.0006	C.I. 0.0003	
	to: 0.0009	to: 0.0005	

* reject data by Q test
C.I.: 95% Confidence Interval

TABLE 3.2.1.1

LINEAR DYNAMIC RANGE DATA:
NaSCN AND ANOVA TABLE
Data January 25, 1986

NaSCN sample (mg) ($\pm$0.001)	area (mm^2) ($\pm$0.05)	best fit area (mm^2)
2.952	102.00	33.10
5.904	186.00	146.61
11.808	421.75	373.62
17.712	617.17	600.63
29.520	1015.00	1054.64
35.424	1190.00	1281.65
41.328	1391.25	1508.66
47.232	1676.50	1735.67
59.040	2178.75	2189.69
64.944	2397.50	2416.70
70.848	2642.50	2643.71
76.752	3036.25	2870.71

Line of best fit:

$$y=-80.40 + 38.45x$$

where y:area (mm^2)
x:sample size (mg)

correlation coefficient: 0.843

ANOVA TABLE

Source	SS	df	MS	F
Crude(Σy^2)	34492904.0	12		
CF($(\Sigma y)^2/n$)	23673325.0	1		
Total(CFM)	10819579.0	11		
Residual	64039.4	10	6403.9	
Regression	10755540.0	1	10755540.0	1679.5

$$F_{1,10,0.05}=4.96$$

Since $F >> F_{1,10,0.05}$ then β_1 is significant and straight line is applicable.

TABLE 3.2.1.2

LINEAR DYNAMIC RANGE DATA:
Na_2SO_4 AND ANOVA TABLE
Data January 25, 1986

Na_2SO_4 sample (mg) ($\pm$0.001)	area (mm^2) ($\pm$0.05)	best fit area (mm^2)
2.9975	114.50	259.63
5.9950	258.75	340.68
11.9900	500.00	502.79
17.9850	753.83	664.89
29.9750	1113.00	989.10
35.9700	1228.50	1151.21
41.9650	1382.50	1313.31
47.9600	1501.50	1475.42
59.9500	1802.50	1779.69
65.9450	1925.00	1961.73
71.9400	2047.50	2123.84
77.9350	2240.00	2285.94

Line of best fit:

$$y=178.58 + 27.04x$$

where y:area (mm^2)
x:sample size (mg)

correlation coefficient: 0.843

ANOVA TABLE

Source	SS	df	MS	F
Crude(Σy^2)	23976599.0	12		
CF($(\Sigma y)^2/n$)	18420411.0	1		
Total(CFM)	5556187.7	11		
Residual	71781.3	10	7178.1	
Regression	5483466.4	1	5483466.4	763.9

$$F_{1,10,0.05}=4.96$$

Since $F >> F_{1,10,0.05}$ then β_1 is significant and straight line is applicable.

TABLE 3.2.1.3

LINEAR DYNAMIC RANGE DATA:
$Na_2S_2O_3$ AND ANOVA TABLE
Data January 25, 1986

$Na_2S_2O_3$ sample (mg) (±0.001)	area (mm^2) (±0.05)	best fit area (mm^2)
2.4932	81.00	226.96
4.9863	189.75	269.76
9.9726	344.00	355.38
14.9589	537.00	440.99
24.9315	715.50	612.22
29.9178	765.00	697.84
34.9041	832.50	783.45
39.8904	922.50	869.07
49.8630	1080.00	1040.30
54.8493	1147.50	1125.91
59.8356	1147.50	1211.53
64.8219	1170.00	1297.14

Line of best fit:

$$y=184.15 + 17.17x$$

where y:area (mm^2)
x:sample size (mg)

correlation coefficient: 0.843

ANOVA TABLE

Source	SS	df	MS	F
Crude(Σy^2)	8259311.3	12		
CF($(\Sigma y)^2/n$)	6648757.5	1		
Total(CFM)	1610553.8	11		
Residual	79797.9	10	7979.8	
Regression	1530755.9	1	1530755.9	191.8

$$F_{1,10,0.05}=4.96$$

Since $F >> F_{1,10,0.05}$ then β_1 is significant and straight line is applicable.

TABLE 3.2.1.4

RESOLUTION VERSUS ELUENT CONCENTRATION
(pH fixed 3.5)

Species	Concentration	t_R ($\pm$0.05)	R_S ($\pm$0.05)
NaSCN	7 mM	6.3	
			0.71
Na_2SO_4		6.8	
			2.00
$Na_2S_2O_3$		8.5	
NaSCN	6 mM	7.2	
			1.37
Na_2SO_4		8.5	
			1.76
$Na_2S_2O_3$		10.7	
NaSCN	5 mM	8.3	
			2.39
Na_2SO_4		11.0	
			2.03
$Na_2S_2O_3$		14.2	

TABLE 3.2.1.5

RESOLUTION VERSUS ELUENT pH
(Concentration fixed 6.02 mM)

Species	pH	t_R ($\pm$0.05)	R_S ($\pm$0.05)
NaSCN	4.10	9.1	
			3.44
Na_2SO_4		11.8	
			2.82
$Na_2S_2O_3$		14.9	
NaSCN	3.80	9.1	
			3.40
Na_2SO_4		12.5	
			3.00
$Na_2S_2O_3$		16.7	
NaSCN	3.60	9.0	
			1.90
Na_2SO_4		12.0	
			2.43
$Na_2S_2O_3$		16.8	
NaSCN	3.55	9.4	
			2.60
Na_2SO_4		13.3	
			2.48
$Na_2S_2O_3$		18.7	
NaSCN	3.40	9.9	
			2.82
Na_2SO_4		14.7	
			2.81
$Na_2S_2O_3$		21.3	

TABLE 3.2.1.6

CALIBRATION CURVE RESULTS: ION EXCHANGE CHROMATOGRAPHY
SILICA BASED TECHNIQUE
December 27, 1985 to January 9, 1986

NaSCN (mg)	Na_2SO_4 (mg)	$Na_2S_2O_3$ (mg)
5.22	5.76	4.86
5.30	5.89	5.34
5.47	5.76	4.52
5.39	5.63	4.02
5.97	5.51	5.68
6.07	5.62	5.97
6.07	5.62	5.97
6.17	5.73	5.56
5.90	4.70	5.86
5.90	4.59	5.86
5.90	4.59	5.86
5.99	4.59	5.64
6.39	5.59	4.45
6.30	5.49	4.31
6.39	5.49	4.02
6.39	5.59	4.02
AVG: 5.93	AVG: 5.64	AVG: 4.44
s : 0.39	s : 0.12	s : 0.47
C.I.:5.71	C.I.:5.56	C.I.:4.05
to: 6.13	to: 5.72	to: 4.83
ACT: 5.90	ACT: 5.99	ACT: 4.88
DIF: 0.3%	DIF: 5.9%	DIF: 9.1%

AVG: average
s : standard deviation
C.I.: 95% confidence interval
ACT: actual result
DIF: difference from actual result

TABLE 3.2.2.1

ELUENTS USED PRELIMINARY POLYMER WORK

Eluent Concentration	Species Eluted (minutes)(±0.05) $NaVO_3$	ADA	Na_3Citrate
1.5 mM $NaHCO_3$/ 1.2 mM Na_2CO_3 (pH 9.8)	6.2	6.1	5.2 -ve 6.4
3.0 mM $NaHCO_3$/ 2.4 mM Na_2CO_3	-ve 6.9	5.4	6.6
4.8 mM $NaHCO_3$/ 4.7 mM Na_2CO_3 (pH 10.0)	3.4 -ve 3.7 -ve 15.5		3.1 -ve 15.0 to 25.0
5.8 mM KOH	-ve 29.0 to -ve 59.0	-ve 15.0 to 30.0	-ve 46.5 to 60.0

TABLE 3.2.2.2

SUBSTITUTED BENZOIC ACID ELUENTS

Eluent Concentration	Species Eluted (minutes)(±0.05) NaCl	$NaVO_3$	ADA	Na_3Citrate
0.5 mM Sulfobenzoic acid (pH 8.8)	xfr 15.8			
0.5 mM Sulfobenzoic acid (pH 10.0)	xfr 9.8			
10 mM Sulfobenzoic acid (pH 8.3)	1.8	np 15	np 25	4.2
10 mM p-Hydroxybenzoic acid (pH 8.6)	1.5	br 5-9.3 -ve 12.2	-ve 10.8	10.1 -ve 11.2 tl16-24
10 mM p-Hydroxybenzoic acid (pH 9.5)	2.2	fr 4.9 -ve 9.4		-ve 8.8 10.2
10 mM p-Hydroxybenzoic acid (pH 10.0)	2.3	4.0 -ve 11.0	-ve 11.0	11.3
5 mM KHP (pH 10.1)	1.9	br 3.8	6-30	5.7
0.52 mM Trimesic acid (pH 9.3)	-ve 1.6 4.0	-ve 6.9	np 30.0	17-25

br: broad
fr: fronting, xfr: extensive fronting
np: no peak after X minutes
tl: tailing

TABLE 3.2.2.3

PHENOL ELUENT

Eluent Concentration	Species Eluted (minutes)(±0.05) NaCl	$NaVO_3$	ADA	Na_3Citrate
10 mM Phenol (pH 10.1)	2.8	7.7	np 45.0	tl 19-25
20 mM Phenol (pH 9.5)	2.8	fr 10.0		tl 21-35
20 mM Phenol (pH 10.0)	2.1	4.1		tl 7.8
30 mM Phenol (pH 9.0)	3.5	fr 18.5 to 21.6		np 25.0
30 mM Phenol (pH 9.5)	2.3	fr 7.1		tl 13-19
30 mM Phenol (pH 10.0)	1.7	3.2	np 40.0	tl 4.3
35 mM Phenol (pH 9.9)		3.6		4.9

fr: fronting
tl: tailing
np: no peak after X minutes

TABLE 3.2.2.4

RESOLUTION VERSUS PHENOL pH
(Concentration fixed 25 mM)

Species	pH (±0.05)	t_R (±0.05)	R_S (±0.05)
Na_2CO_3	10.05	2.00	
			1.56
Na_2SO_4		2.85	
			1.14
$NaVO_3$		3.35	
			2.00
$Na_2S_2O_3$		4.20	
			3.07
Na_3Citrate		tl 7.50	
			2.00
NaSCN		9.70	
Na_2CO_3	10.15	2.05	
			1.42
Na_2SO_4		2.90	
			1.14
$NaVO_3$		3.40	
			1.89
$Na_2S_2O_3$		4.25	
			2.77
Na_3Citrate		tl 7.50	
			1.76
NaSCN		9.65	
Na_2CO_3	10.22	2.05	
			1.20
Na_2SO_4		2.65	
			1.00
$NaVO_3$		3.05	
			1.88
$Na_2S_2O_3$		3.80	
			2.71
Na_3Citrate		6.10	
			3.21
NaSCN		9.15	

tl: tailing

TABLE 3.2.2.5

RESOLUTION VERSUS PHENOL CONCENTRATION
(pH fixed 10.15 mM)

Species	Concentration	t_R ($\pm$0.05)	R_S ($\pm$0.05)
Na_2CO_3	25 mM	2.05	
			1.42
Na_2SO_4		2.90	
			1.14
$NaVO_3$		3.40	
			1.89
$Na_2S_2O_3$		4.25	
			2.77
Na_3Citrate		tl 7.50	
			1.76
NaSCN		9.65	
Na_2CO_3	30 mM	1.80	
			1.00
Na_2SO_4		2.20	
			1.00
$NaVO_3$		2.60	
			0.89
$Na_2S_2O_3$		3.00	
			1.93
Na_3Citrate		4.42	
			3.03
NaSCN		7.20	
Na_2CO_3	35 mM	1.70	
			0.67
Na_2SO_4		2.00	
			1.06
$NaVO_3$		2.45	
			0.59
$Na_2S_2O_3$		2.72	
			1.43
Na_3Citrate		3.73	
			3.56
NaSCN		6.90	

TABLE 3.2.2.6

LINEAR DYNAMIC RANGE RESOLUTION DATA

Species Eluted	Aliquot (mL) (±0.005)	t_R (min.) (±0.05)	R_S (±0.05)
Na_2CO_3	0.01	2.05	
			2.50
Na_2SO_4		2.80	
			2.67
$NaVO_3$		3.10	
			4.50
$Na_2S_2O_3$		4.20	
			6.18
Na_3Citrate		7.60	
NaSCN		np	
Na_2CO_3	0.02	1.90	
			2.15
Na_2SO_4		2.60	
			2.00
$NaVO_3$		3.10	
			3.10
$Na_2S_2O_3$		4.05	
			4.85
Na_3Citrate		7.20	
NaSCN		np	
Na_2CO_3	0.03	2.05	
			1.75
Na_2SO_4		2.75	
			1.33
$NaVO_3$		3.15	
			2.13
$Na_2S_2O_3$		4.00	
			3.81
Na_3Citrate		6.95	
NaSCN		np	

np: no peak

TABLE 3.2.2.6 (cont'd)

LINEAR DYNAMIC RANGE RESOLUTION DATA

Species Eluted	Aliquot (mL) (±0.005)	t_R (min.) (±0.05)	R_S (±0.05)
Na_2CO_3	0.50	1.95	
			1.52
Na_2SO_4		2.60	
			1.31
$NaVO_3$		3.00	
			2.79
$Na_2S_2O_3$		3.85	
			3.35
Na_3Citrate		6.45	
			3.33
NaSCN		9.45	
Na_2CO_3	1.00	2.00	
			1.30
Na_2SO_4		2.65	
			0.82
$NaVO_3$		3.00	
			2.00
$Na_2S_2O_3$		3.90	
			2.45
Na_3Citrate		6.35	
			2.61
NaSCN		8.30	
Na_2CO_3	2.00	2.15	
			1.04
Na_2SO_4		2.80	
			0.76
$NaVO_3$		3.20	
			1.40
$Na_2S_2O_3$		3.90	
			2.05
Na_3Citrate		6.15	
			2.21
NaSCN		9.25	

TABLE 3.2.2.6 (cont'd)

LINEAR DYNAMIC RANGE RESOLUTION DATA

Species Eluted	Aliquot (mL) (±0.005)	t_R (min.) (±0.05)	R_S (±0.05)
Na_2CO_3	3.00	os	
Na_2SO_4		2.60	
			0.53
$NaVO_3$		3.05	
			0.89
$Na_2S_2O_3$		3.70	
			1.60
$Na_3Citrate$		5.90	
			2.07
NaSCN		9.00	
Na_2CO_3	5.00	os	
Na_2SO_4		2.55	
			0.33
$NaVO_3$		2.90	
			0.70
$Na_2S_2O_3$		3.55	
			1.48
$Na_3Citrate$		5.85	
			1.56
NaSCN		8.70	
Na_2CO_3	6.00	os	
Na_2SO_4		2.65	
			0.30
$NaVO_3$		3.00	
			0.65
$Na_2S_2O_3$		3.70	
			1.42
$Na_3Citrate$		6.10	
			1.19
NaSCN		8.45	

os: offscale

TABLE 3.2.2.7

LINEAR DYNAMIC RANGE DATA
Na_2CO_3 AND ANOVA TABLE FOR POLYMER BASED TECHNIQUE
(April 3, 1986)

Na_2CO_3 sample (µg)	area (mm^2)	best fit area (mm^2)
250.20	7050.00	7196.93
125.10	4323.00	4282.30
62.55	3330.00	2824.98
37.53	2622.00	2242.06
25.02	1596.00	1950.60
12.51	1235.00	1659.13

Line of best fit:

$$y=1367.67 + 23.30x$$

where y:area (mm^2)
x:sample size (mg)

$t=25.792$

$t_{4,0.025}=2.776$

Since $t > t_{4,0.025}$ do not reject $ß_0$

ANOVA TABLE

Source	SS	df	MS	F
Crude($\sum y^2$)	90427054.0	6		
CF($(\sum y)^2/n$)	67710722.7	1		
Total(CFM)	22716331.3	5		
Residual	728267.4	4	182066.8	
Regression	21988064.0	1	21988064.0	120.8

$F_{1,4,0.05}=7.71$

Since $F >> F_{1,4,0.05}$ then $ß_1$ is significant and straight line is applicable.

TABLE 3.2.2.8

LINEAR DYNAMIC RANGE DATA
Na_2SO_4 AND ANOVA TABLE FOR POLYMER BASED TECHNIQUE
(April 3, 1986)

Na_2SO_4 sample (µg)	area (mm^2)	best fit area (mm^2)
30.2400	6822.50	6212.59
25.2000	5190.00	5136.53
15.1200	2096.50	2984.41
10.0800	1421.00	1908.35
5.0400	508.00	832.29
2.5200	324.00	294.26
0.1512	169.50	-211.49
0.1008	117.00	-222.25
0.0504	53.20	-233.01

Line of best fit:

$$y=-243.77 + 213.50x$$

where y:area (mm^2)
x:sample size (mg)

$t=-47.310$

$t_{7,0.025}=2.365$

Since $t > t_{7,0.025}$ do not reject $ß_0$

ANOVA TABLE

Source	SS	df	MS	F
Crude($\sum y^2$)	80305449.0	9		
CF($(\sum y)^2/n$)	30994087.0	1		
Total(CFM)	49311362.0	8		
Residual	1848949.5	7	264135.6	
Regression	47462412.5	1	47462412.5	179.7

$F_{1,7,0.05}=5.59$

Since $F >> F_{1,7,0.05}$ then $ß_1$ is significant and straight line is applicable.

TABLE 3.2.2.9

LINEAR DYNAMIC RANGE DATA
$NaVO_3$ AND ANOVA TABLE FOR POLYMER BASED TECHNIQUE
(April 3, 1986)

$NaVO_3$ sample (µg)	area (mm^2)	best fit area (mm^2)
44.7600	5842.50	5736.45
37.3000	5067.50	4752.98
22.3800	2397.50	2786.04
14.9200	1421.00	1802.58
7.4600	561.20	819.58
3.7300	254.00	327.37
0.2238	136.00	-134.86
0.1492	80.75	-144.69
0.0746	30.00	-154.53

Line of best fit:

$$y=-164.33 + 131.83x$$

where y:area (mm^2)
x:sample size (mg)

$t=-21.551$

$t_{7,0.025}=2.365$

Since $t > t_{7,0.025}$ do not reject $ß_0$

ANOVA TABLE

Source	SS	df	MS	F
Crude(Σy^2)	67986987.8	9		
CF($(\Sigma y)^2/n$)	27704256.8	1		
Total(CFM)	40282731.0	8		
Residual	636872.8	7	90981.8	
Regression	39645858.1	1	39645858.1	435.8

$$F_{1,7,0.05}=5.59$$

Since $F >> F_{1,7,0.05}$ then $ß_1$ is significant and straight line is applicable.

TABLE 3.2.2.10

LINEAR DYNAMIC RANGE DATA
$Na_2S_2O_3$ AND ANOVA TABLE FOR POLYMER BASED TECHNIQUE
(April 3, 1986)

$Na_2S_2O_3$ sample (µg)	area (mm^2)	best fit area (mm^2)
30.3600	4117.50	4578.91
25.3000	4162.50	3843.09
15.1800	2742.50	2371.45
10.1200	1764.00	1635.63
5.0600	800.00	899.82
2.5300	336.00	531.91
0.1518	202.65	186.07
0.1012	136.80	178.71
0.0506	135.00	171.36

Line of best fit:

$$y=164.00 + 146.00x$$

where y:area (mm^2)
x:sample size (mg)

$t=31.828$

$t_{7,0.025}=2.365$

Since $t > t_{7,0.025}$ do not reject $ß_0$

ANOVA TABLE

Source	SS	df	MS	F
Crude(Σy^2)	45744117.0	9		
CF($(\Sigma y)^2/n$)	23030241.0	1		
Total(CFM)	22713876.0	8		
Residual	520770.2	7	74395.7	
Regression	22193105.8	1	22193105.8	298.3

$$F_{1,7,0.05}=5.59$$

Since $F >> F_{1,7,0.05}$ then $ß_1$ is significant and straight line is applicable.

TABLE 3.2.2.11

LINEAR DYNAMIC RANGE DATA
$Na_3Citrate$ AND ANOVA TABLE FOR POLYMER BASED TECHNIQUE
(April 3, 1986)

$Na_3Citrate$ sample (µg)	area (mm^2)	best fit area (mm^2)
300.8400	7248.75	8618.11
250.7000	7800.00	7351.24
150.4200	5850.00	4817.50
100.2800	4800.00	3550.62
50.1400	2870.00	2283.75
25.0700	1285.20	1650.32
1.5042	711.00	1054.89
1.0028	553.25	1042.22
0.5014	280.00	1029.55

Line of best fit:

$$y=1016.88 + 25.27x$$

where y:area (mm^2)
x:sample size (mg)

$t=19.838$

$t_{7,0.025}=2.365$

Since $t > t_{7,0.025}$ do not reject $ß_0$

ANOVA TABLE

Source	SS	df	MS	F
Crude($\sum y^2$)	181425522.2	9		
CF(($\sum y)^2/n$)	109538551.5	1		
Total(CFM)	71886970.7	8		
Residual	6099709.3	7	871387.0	
Regression	65787261.4	1	65787261.4	75.5

$$F_{1,7,0.05}=5.59$$

Since $F >> F_{1,7,0.05}$ then $ß_1$ is significant and straight line is applicable.

TABLE 3.2.2.12

LINEAR DYNAMIC RANGE DATA
NaSCN AND ANOVA TABLE FOR POLYMER BASED TECHNIQUE
(April 3, 1986)

NaSCN sample (µg)	area (mm^2)	best fit area (mm^2)
28.9200	2665.00	2640.00
24.1000	2267.50	2155.79
14.4600	1012.50	1187.37
9.6400	545.10	703.16
4.8200	287.00	218.95
2.4100	105.00	-23.16

Line of best fit:

$$y=-265.26 + 100.46x$$

where y:area (mm^2)
x:sample size (mg)

$t=-34.748$

$t_{7,0.025}=2.365$

Since $t > t_{7,0.025}$ do not reject $ß_0$

ANOVA TABLE

Source	SS	df	MS	F
Crude($\sum y^2$)	13659465.5	6		
CF($(\sum y)^2/n$)	7893883.4	1		
Total(CFM)	5765582.1	5		
Residual	300812.0	4	75203.0	
Regression	5464770.1	1	5464770.1	72.7

$$F_{1,4,0.05}=7.71$$

Since $F >> F_{1,4,0.05}$ then $ß_1$ is significant and straight line is applicable.

TABLE 3.2.2.13

CALIBRATION CURVE RESULTS: ION EXCHANGE POLYMER BASED TECHNIQUE
April 8, 1986 to April 18, 1986

Na_2CO_3 (µg)	Na_2SO_4 (µg)	$NaVO_3$ (µg)
125.0000	5.4611	7.5923
121.1469	5.4611	8.2390
97.5941	5.5606	8.2390
99.0412	5.3511	8.4315
100.4884	5.5606	8.2390
133.5043	5.6654	8.2390
125.0427	5.7070	8.4432
94.0171	5.7070	8.4432
124.0598	4.8849	8.2422
143.8392	5.9910	7.4210
142.2308	5.2272	7.4210
112.9301	5.2272	7.8409
168.3147	5.5390	7.6309
131.0296	5.3831	7.4237
127.9185	4.2927	7.6566
132.5852	4.2927	7.4237
117.1037	4.1503	7.4237
153.1728	4.1503	7.7551
158.1111	4.6609	7.7551
155.6420	4.9483	7.7551
153.1728	4.8046	7.7551
170.9874	4.8046	------
173.3403	------	AVG: 7.6232
173.3403	AVG: 4.8826	s : 0.2790
173.3403	s : 0.5873	C.I.: 7.4546
--------	C.I.: 4.5436	to : 7.7918
AVG:136.2781	to : 5.2217	ACT: 7.5110
s : 24.8839	ACT: 5.0375	DIF: 1.49%
C.I.:126.0260	DIF: 3.07%	
to:146.5303		
ACT:125.0130		
DIF:9.01%		

AVG: average
s : standard deviation
C.I.: 95% confidence interval
ACT: actual result
DIF: difference from actual result

TABLE 3.2.2.14

CALIBRATION CURVE RESULTS: ION EXCHANGE POLYMER BASED TECHNIQUE
April 8, 1986 to April 18, 1986

$Na_2S_2O_3$ (µg)	$Na_3Citrate$ (µg)	NaSCN (µg)
4.6911	57.3878	4.8898
4.3855	44.3776	5.2220
4.3855	44.3776	4.3585
4.3855	54.0714	4.8898
4.5383	50.7551	4.6684
4.5383	64.1620	4.8898
5.0826	66.7570	4.3363
5.1980	63.3709	5.5981
5.1980	62.6430	3.6644
5.3135	61.3342	4.2169
6.1844	58.0054	4.4413
5.9675	66.6332	4.9574
6.1844	51.4158	4.1832
6.1844	61.6011	5.0079
4.9541	66.7924	4.0515
5.3007	66.7924	4.6781
5.4740	69.7978	5.7995
5.6473	58.8741	4.0741
5.1858	54.7179	5.0000
5.1858	63.3451	4.4048
5.1858	59.3778	4.4048
5.1858	56.0561	5.6720
5.0394	56.0561	4.9463
5.0394	57.8084	4.9463
5.0394	62.8026	4.9463
5.2612	55.0047	------
------	-------	AVG: 4.7299
AVG: 5.1821	AVG: 59.0122	s : 0.5149
s : 0.5214	s : 6.4904	C.I.: 4.5167
C.I.: 4.9715	C.I.: 56.3901	to: 4.9431
to: 5.3928	to: 61.6343	ACT: 5.1220
ACT: 5.0475	ACT: 50.0395	DIF: 7.66%
DIF: 2.79%	DIF: 18.02%	

AVG: average
s : standard deviation
C.I.: 95% confidence interval
ACT: actual result
DIF: difference from actual result

TABLE 3.2.2.15

STANDARD ADDITION RESULTS: ION EXCHANGE POLYMER BASED TECHNIQUE
April 8, 1986 to April 18, 1986

	Na_2CO_3 (mg)	Na_2SO_4 (mg)	$NaVO_3$ (mg)
	27.7163	0.5383	0.7253
	31.1676	1.6792	0.7187
	31.4154	1.3274	0.9674
	18.7938	0.5742	0.6512
	15.2794	0.7742	1.2926
	24.8256	0.5476	1.1054
	44.5146	1.7548	1.2099
	41.8687	1.9590	0.7967
	44.3396	0.9116	0.8697
	35.1080	1.1754	0.9191
	-------	0.6941	0.7580
AVG:	24.8664	0.9655	1.0515
s :	6.0486	0.5855	1.1598
C.I.:	18.5177	0.6378	0.6973
to :	31.2150	1.4105	2.1477
ACT:	12.5013	0.8965	1.8425
DIF:	98.91%	0.5869	1.7329
		2.5983	1.7942
		------	------
	AVG:	1.0011	AVG: 0.9230
	s :	0.4534	s : 0.2033
	C.I.:	0.7680	C.I.: 0.8073
	to :	1.2342	to : 1.0388
	ACT:	0.5038	ACT: 0.7511
	DIF:	98.73%	DIF: 22.89%

AVG: average
s : standard deviation
C.I.: 95% confidence interval
ACT: actual result
DIF: difference from actual result

TABLE 3.2.2.16

STANDARD ADDITION RESULTS: ION EXCHANGE
POLYMER BASED TECHNIQUE
April 8, 1986 to April 18, 1986

$Na_2S_2O_3$ (mg)	$Na_3Citrate$ (mg)	NaSCN (mg)
0.5066	5.9109	0.2917
0.9524	4.9832	0.4795
0.5242	7.2806	0.5567
0.5779	5.8870	0.3340
0.4759	7.3588	0.3461
0.5590	5.3123	0.3234
0.7420	6.8123	0.2434
0.9243	8.9398	0.2039
0.6391	5.0535	0.4292
0.6981	6.7434	0.3915
0.7877	9.0124	0.3463
0.5587	5.6044	0.3940
0.6286	7.0842	0.2899
0.4604	8.9242	0.2627
0.5762	16.1552	0.4728
0.6269	13.4476	0.4802
0.4327	11.7911	0.4316
1.4839	4.0938	0.7412
------	------	------
AVG:0.6277	AVG: 6.7791	AVG: 0.3692
s :0.1468	s : 1.3686	s : 0.0940
C.I.:0.5522	C.I.: 5.9890	C.I.: 0.3209
to :0.7032	to : 7.5692	to : 0.4176
ACT:0.5042	ACT: 5.0040	ACT: 0.4176
DIF:24.50%	DIF: 35.47%	DIF: 27.91%

AVG: average
s : standard deviation
C.I.: 95% confidence interval
ACT: actual result
DIF: difference from actual result

Figure 3.1.1 The ion pair HPLC analysis of Stretford liquor prior to spiking with Na_2SO_4 and $Na_2S_2O_3$.

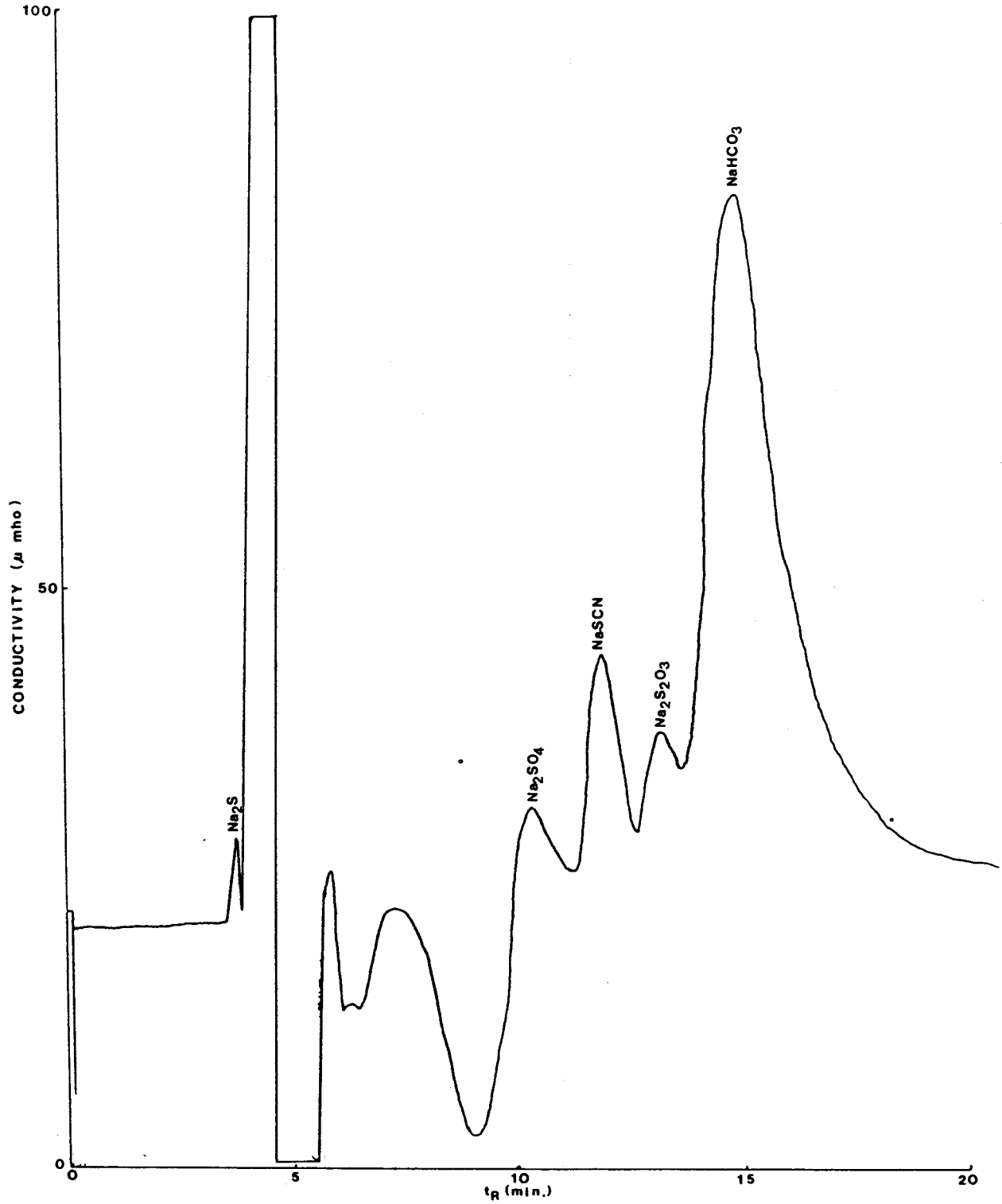

100
50
0
CONDUCTIVITY (μ mho)
Na2S
Na2SO4
NaSCN
Na2S2O3
NaHCO3
0
5
10
15
20
tR (min.)

Figure 3.1.2 The ion pair HPLC analysis of Stretford liquor after spiking with Na_2SO_4 and $Na_2S_2O_3$.

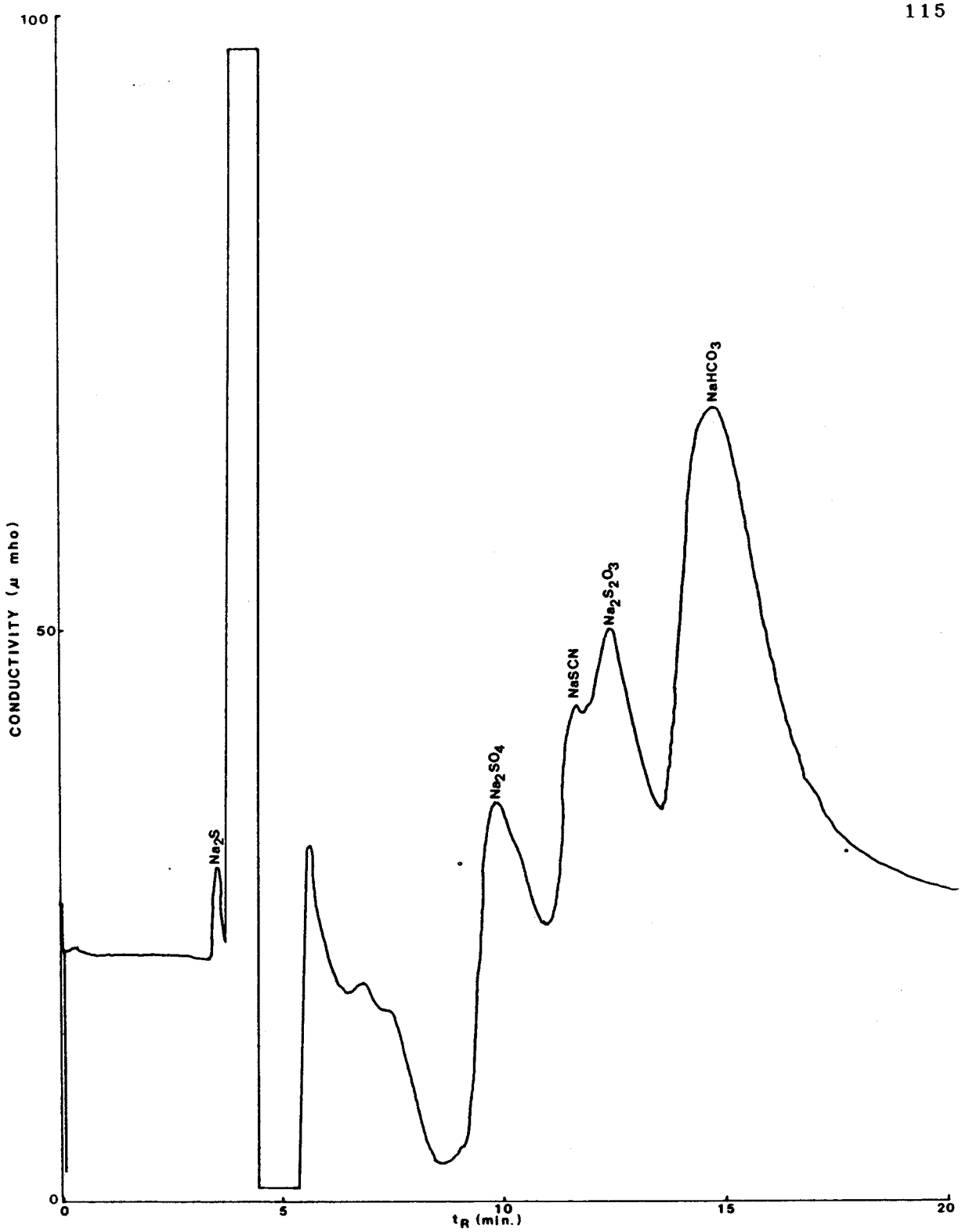

100
50
0
CONDUCTIVITY (μ mho)
Na2S
Na2SO4
NaSCN
Na2S2O3
NaHCO3
0
5
10
15
20
tR (min.)

Figure 3.2.1.1 Linear dynamic range for NaSCN by ion exchange silica based technique.

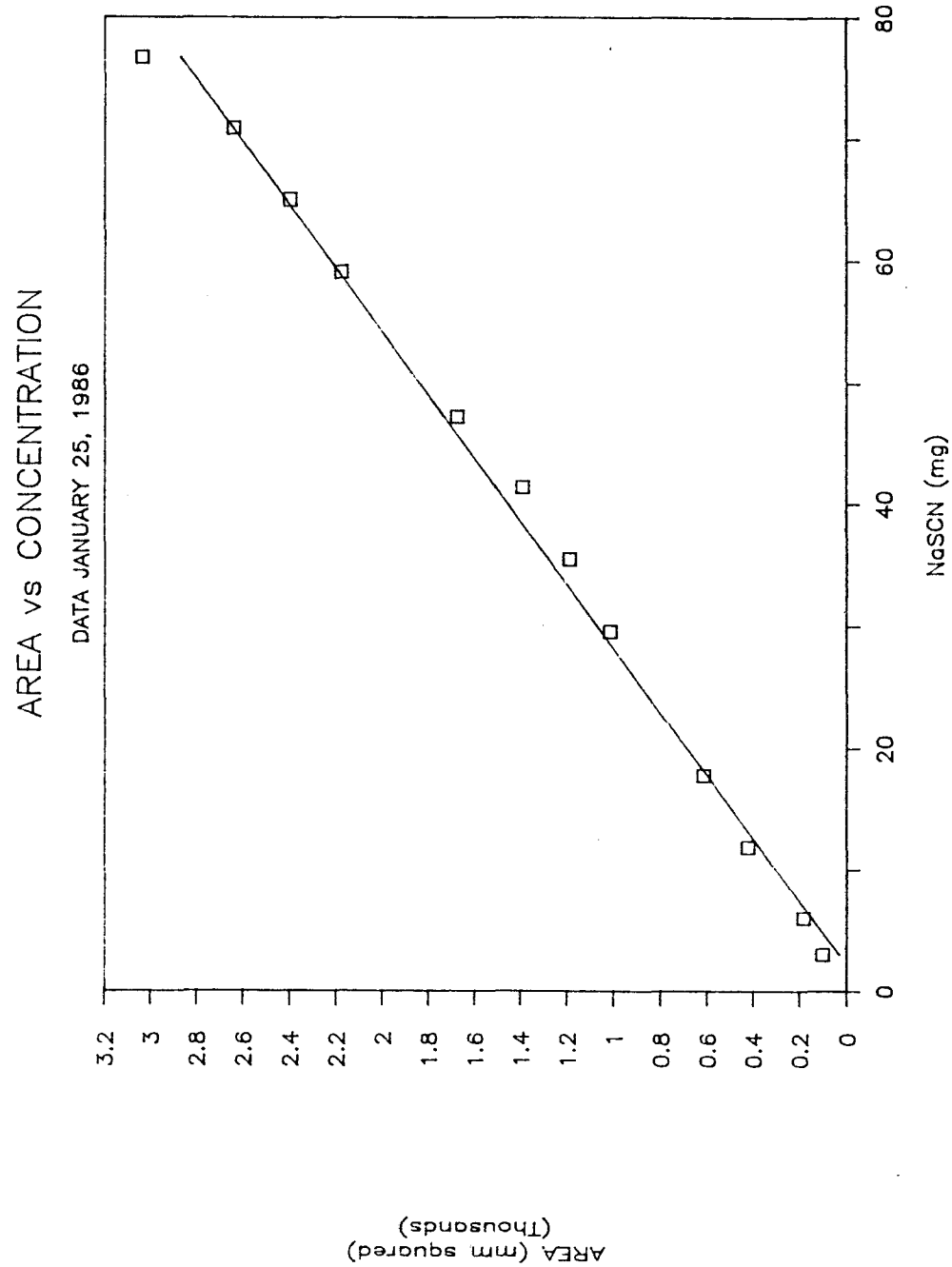

AREA vs CONCENTRATION
DATA JANUARY 25, 1986
AREA (mm squared)
(Thousands)
NaSCN (mg)
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
2
2.2
2.4
2.6
2.8
3
3.2
0
20
40
60
80

Figure 3.2.1.2 Linear dynamic range for Na_2SO_4 by ion exchange silica based technique.

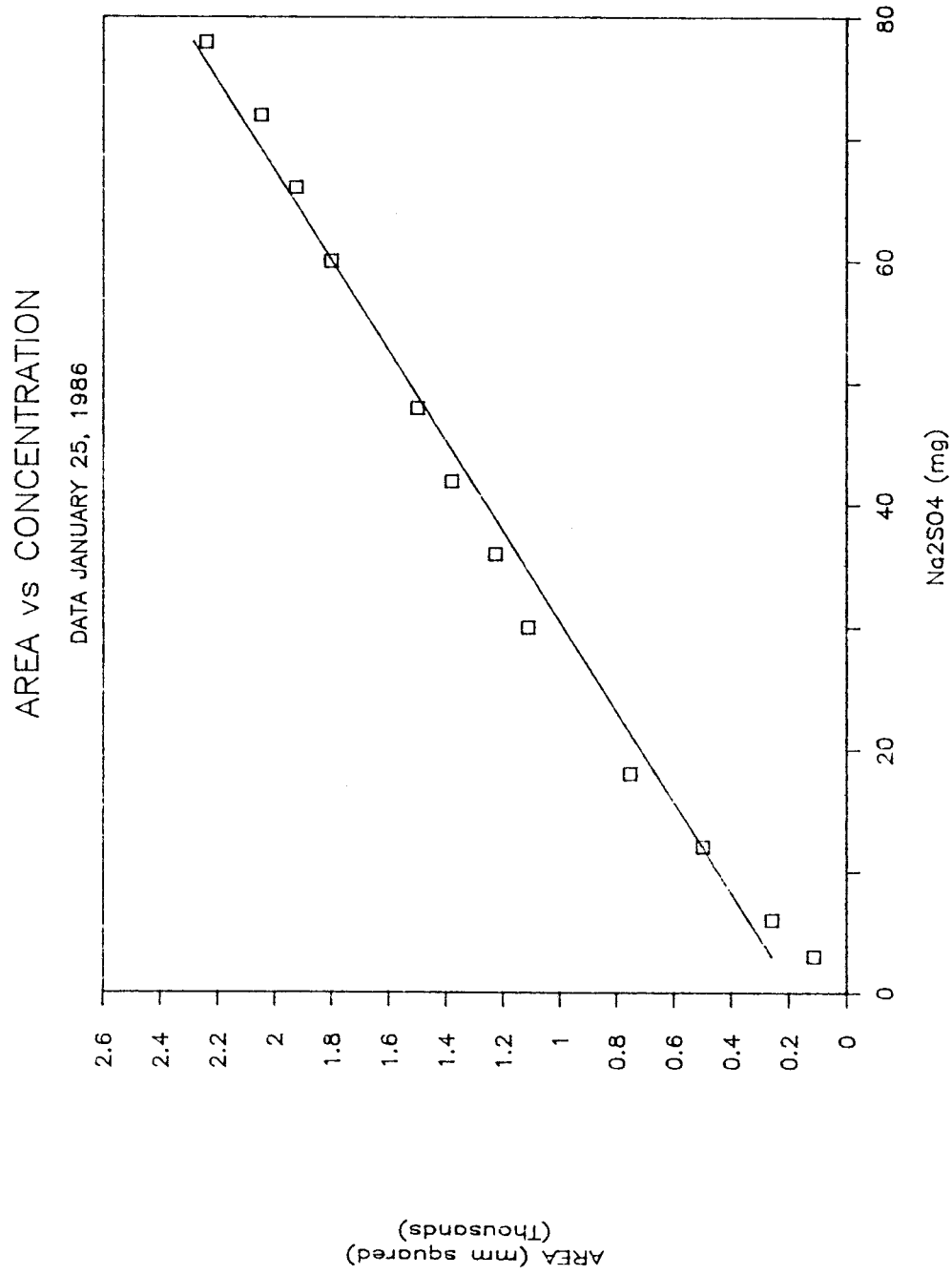

AREA vs CONCENTRATION
DATA JANUARY 25, 1986
AREA (mm squared)
(Thousands)
2.6
2.4
2.2
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
0
20
40
60
80
Na2SO4 (mg)

Figure 3.2.1.3 Linear dynamic range for $Na_2S_2O_3$ by ion exchange silica based technique.

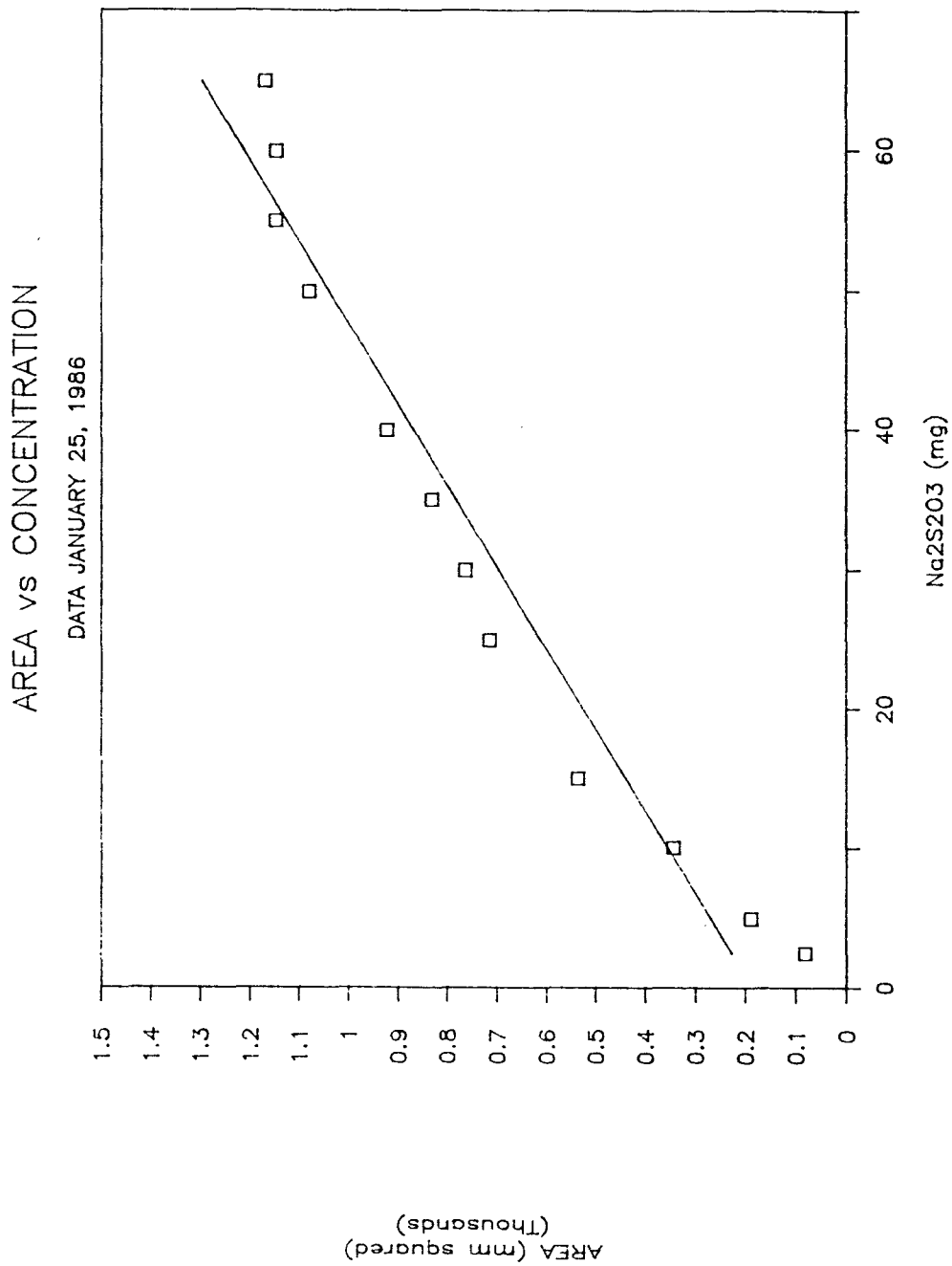

AREA vs CONCENTRATION
DATA JANUARY 25, 1986
AREA (mm squared)
(Thousands)
1.5
1.4
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
20
40
60
Na2S2O3 (mg)

Figure 3.2.1.4 Response Surface for Resolution between NaSCN and Na_2SO_4

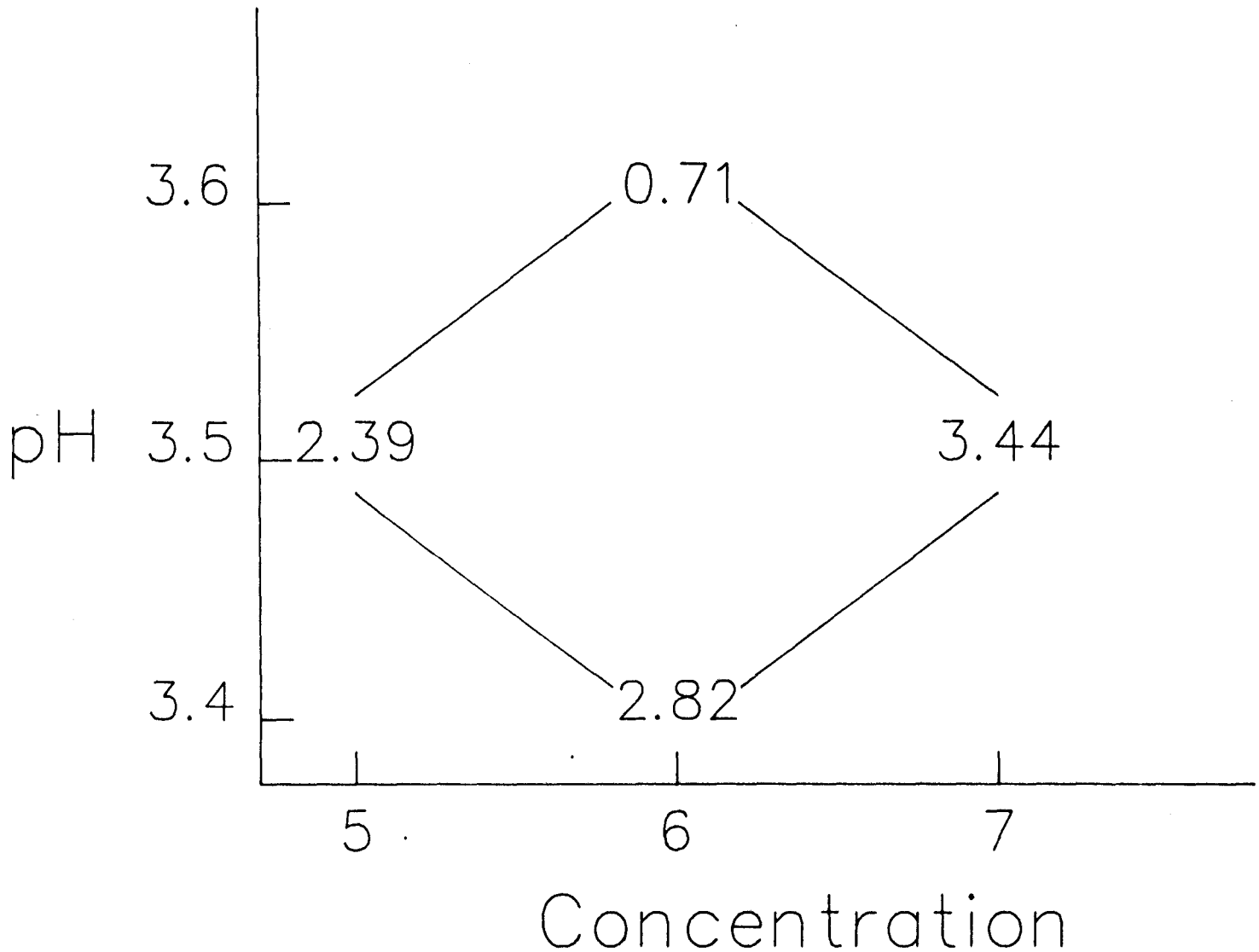

3.6
0.71
pH
3.5
2.39
3.44
3.4
2.82
5
6
7
Concentration

Figure 3.2.1.5 The ion exchange HPLC analysis of Stretford liquors using silica based technique.

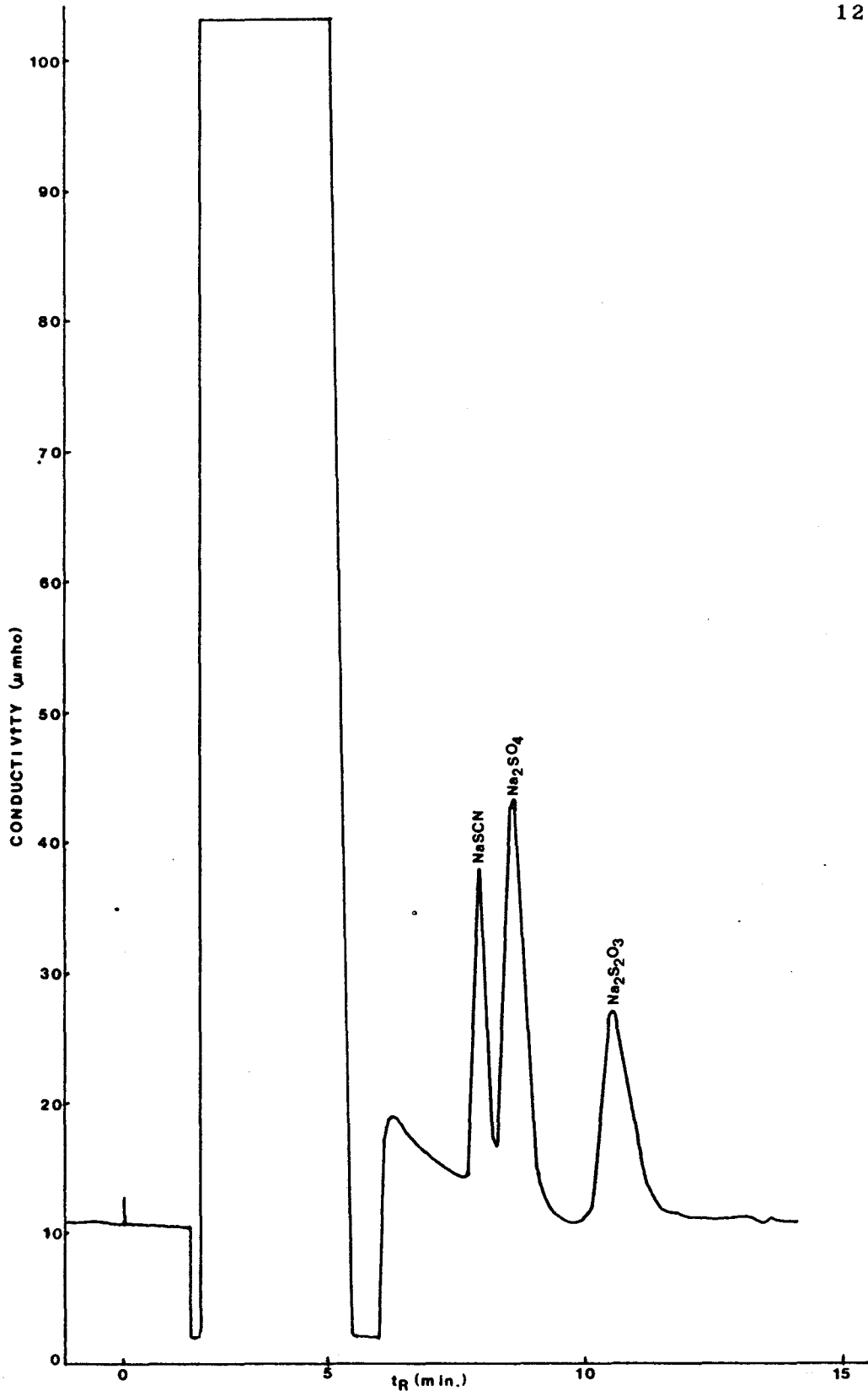

CONDUCTIVITY (μmho)
100
90
80
70
60
50
40
30
20
10
0
0
5
10
15
t_R (min.)
NaSCN
Na_2SO_4
$Na_2S_2O_3$

Figure 3.2.2.1 The ion exchange HPLC analysis of a calibration solution using polymer based technique.

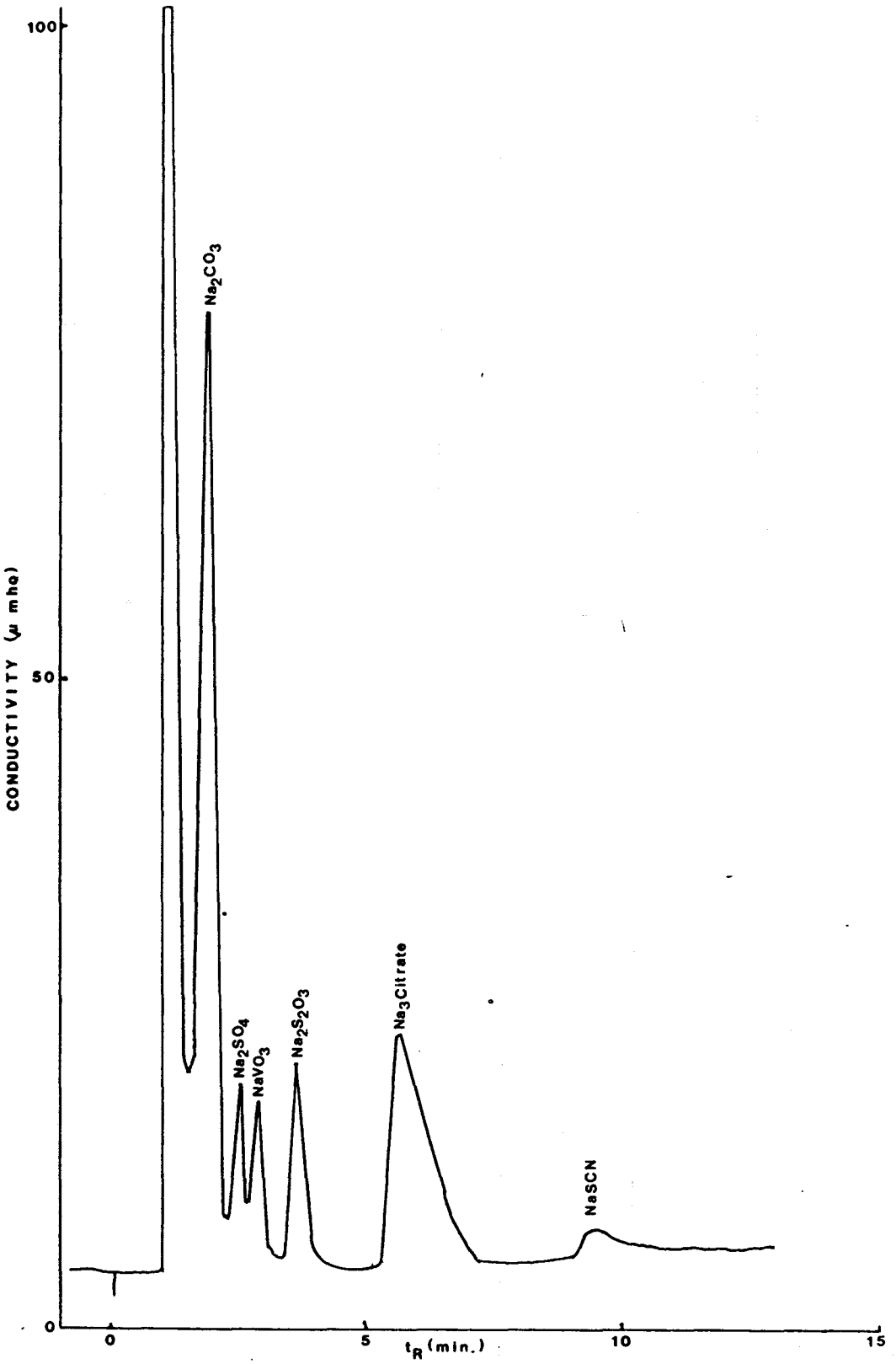

100
50
0
CONDUCTIVITY (μ mho)
Na_2CO_3
Na_2SO_4
$NaVO_3$
$Na_2S_2O_3$
$Na_3Citrate$
NaSCN
0
5
10
15
t_R (min.)

Figure 3.2.2.2 The ion exchange HPLC analysis of a synthetic Stretford solution (without ADA) using polymer based technique.

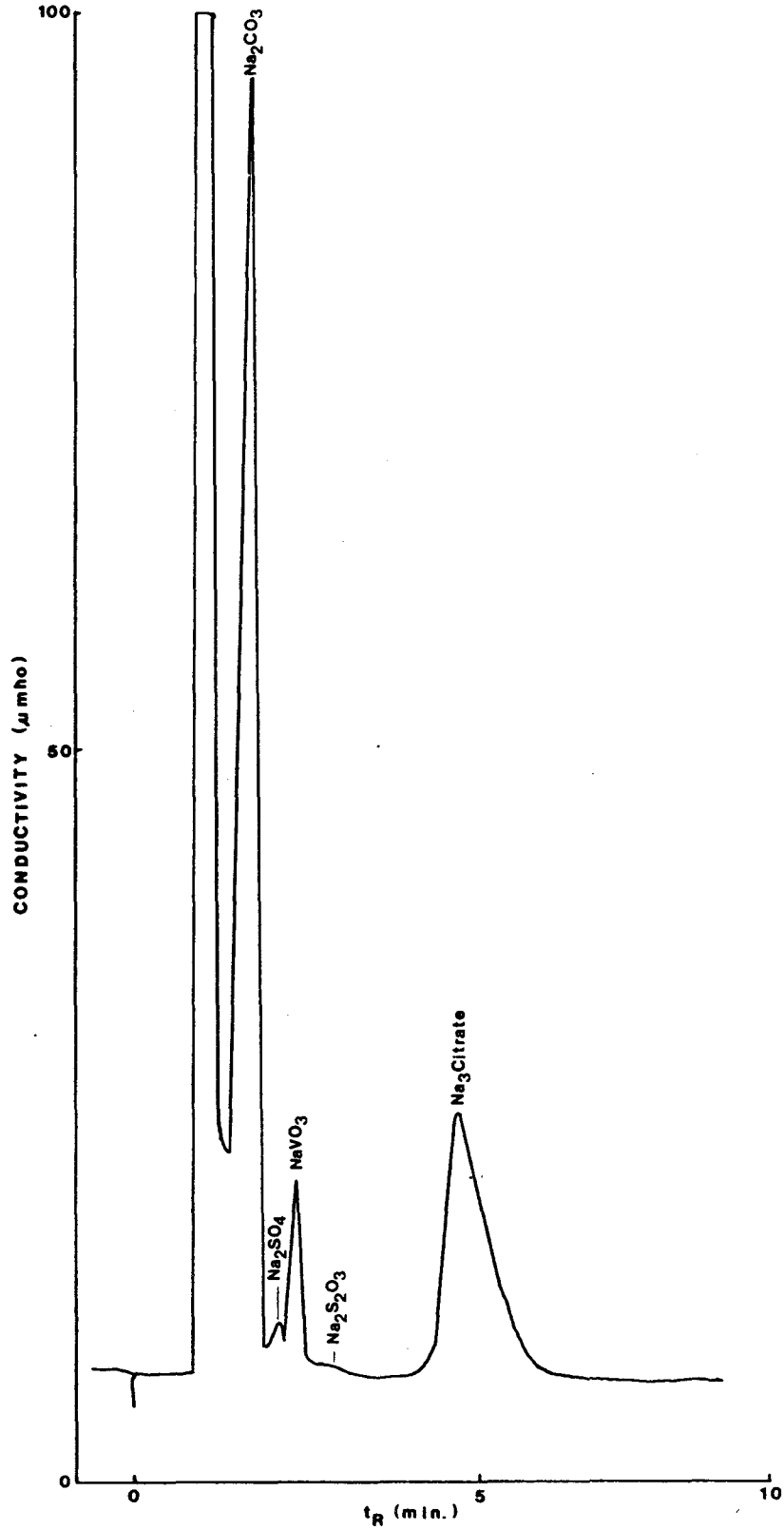

100
50
0
CONDUCTIVITY (μmho)
Na_2CO_3
Na_2SO_4
$NaVO_3$
$Na_2S_2O_3$
$Na_3Citrate$
0
5
10
t_R (min.)

Figure 3.2.2.3 Linear dynamic range for Na_2CO_3 by ion exchange polymer based technique.

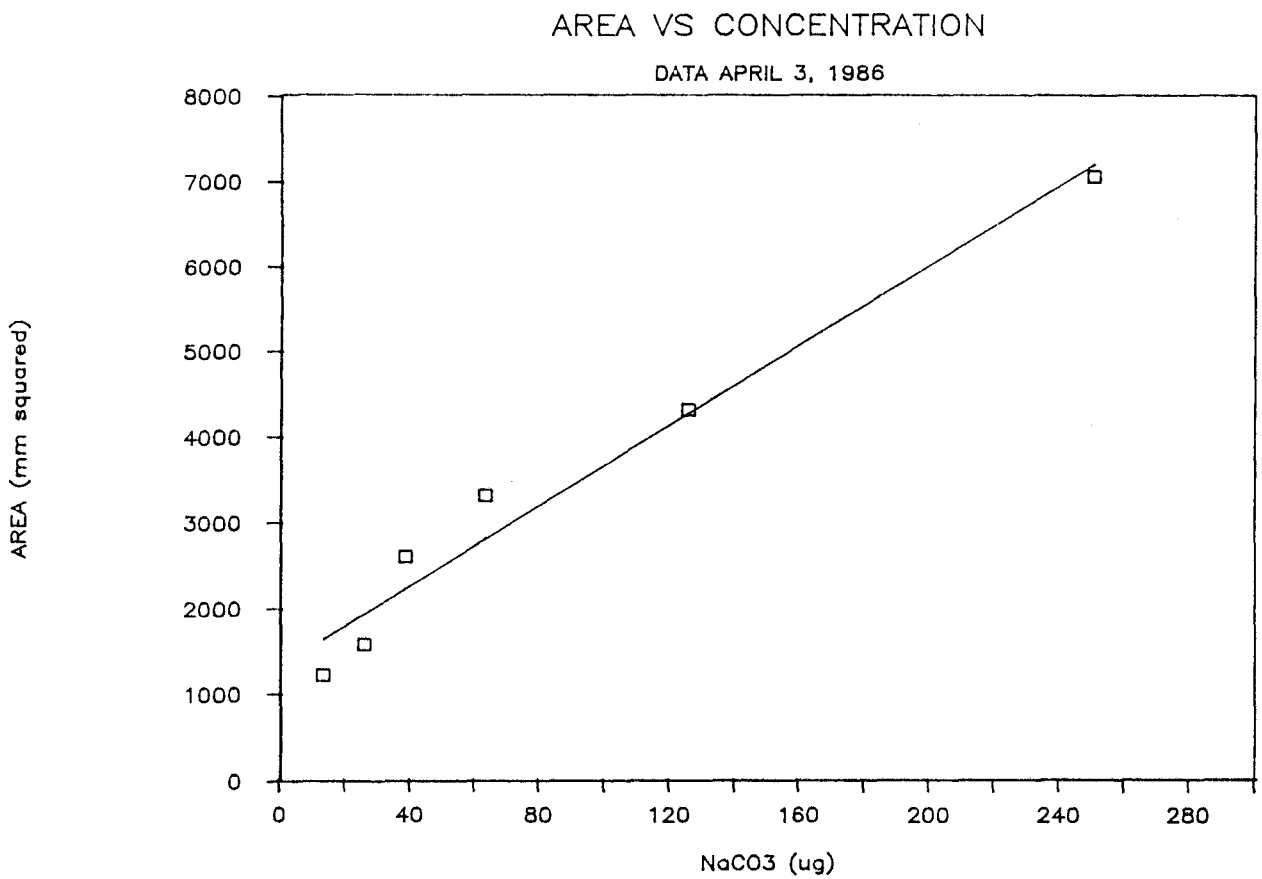

AREA VS CONCENTRATION
DATA APRIL 3, 1986
AREA (mm squared)
8000
7000
6000
5000
4000
3000
2000
1000
0
0
40
80
120
160
200
240
280
NaCO3 (ug)

Figure 3.2.2.4 Linear dynamic range for Na_2SO_4 by ion exchange polymer based technique.

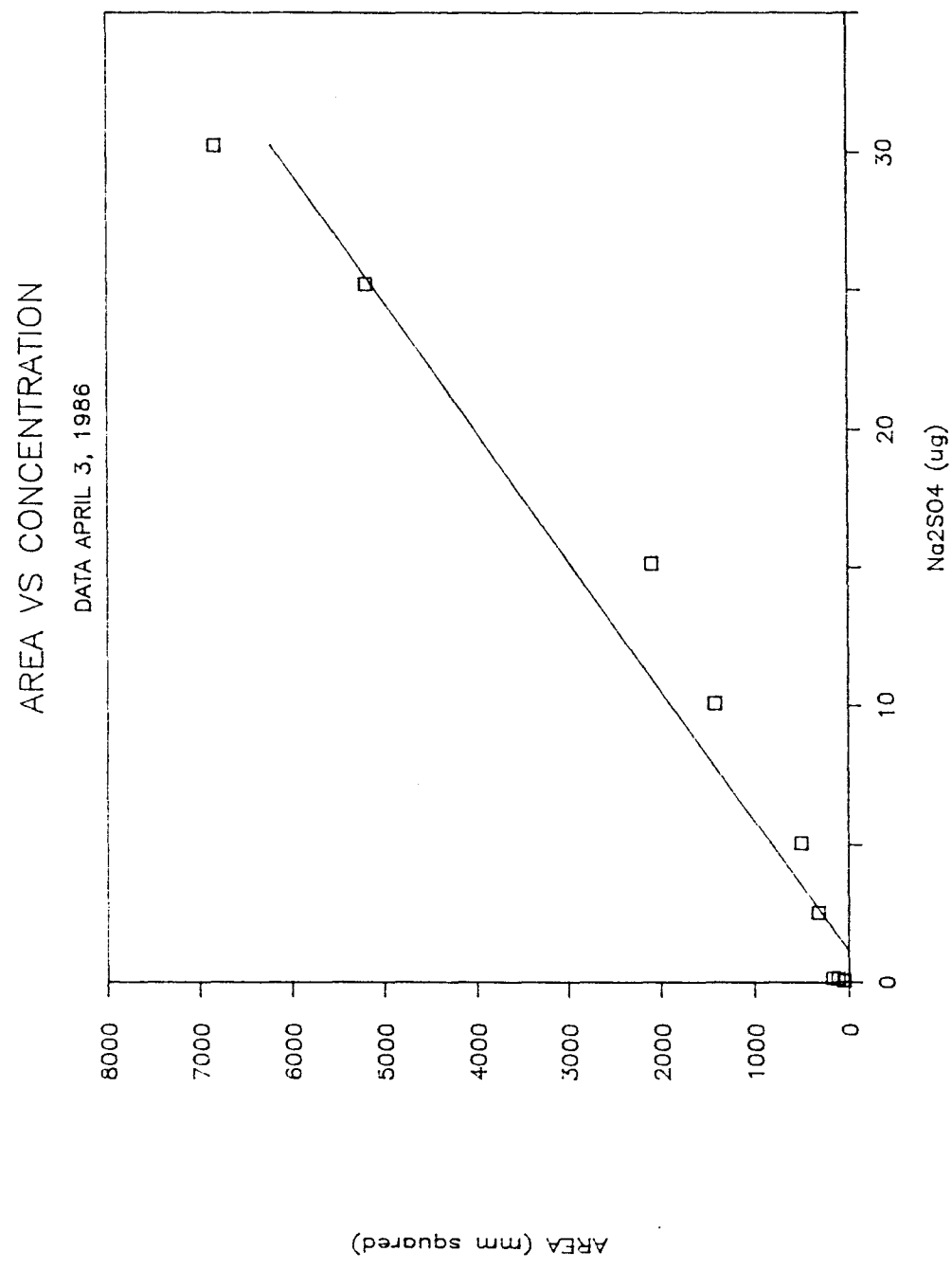

AREA VS CONCENTRATION
DATA APRIL 3, 1986
AREA (mm squared)
8000
7000
6000
5000
4000
3000
2000
1000
0
0
10
20
30
Na2SO4 (ug)

Figure 3.2.2.5 Linear dynamic range for $NaVO_3$ by ion exchange polymer based technique.

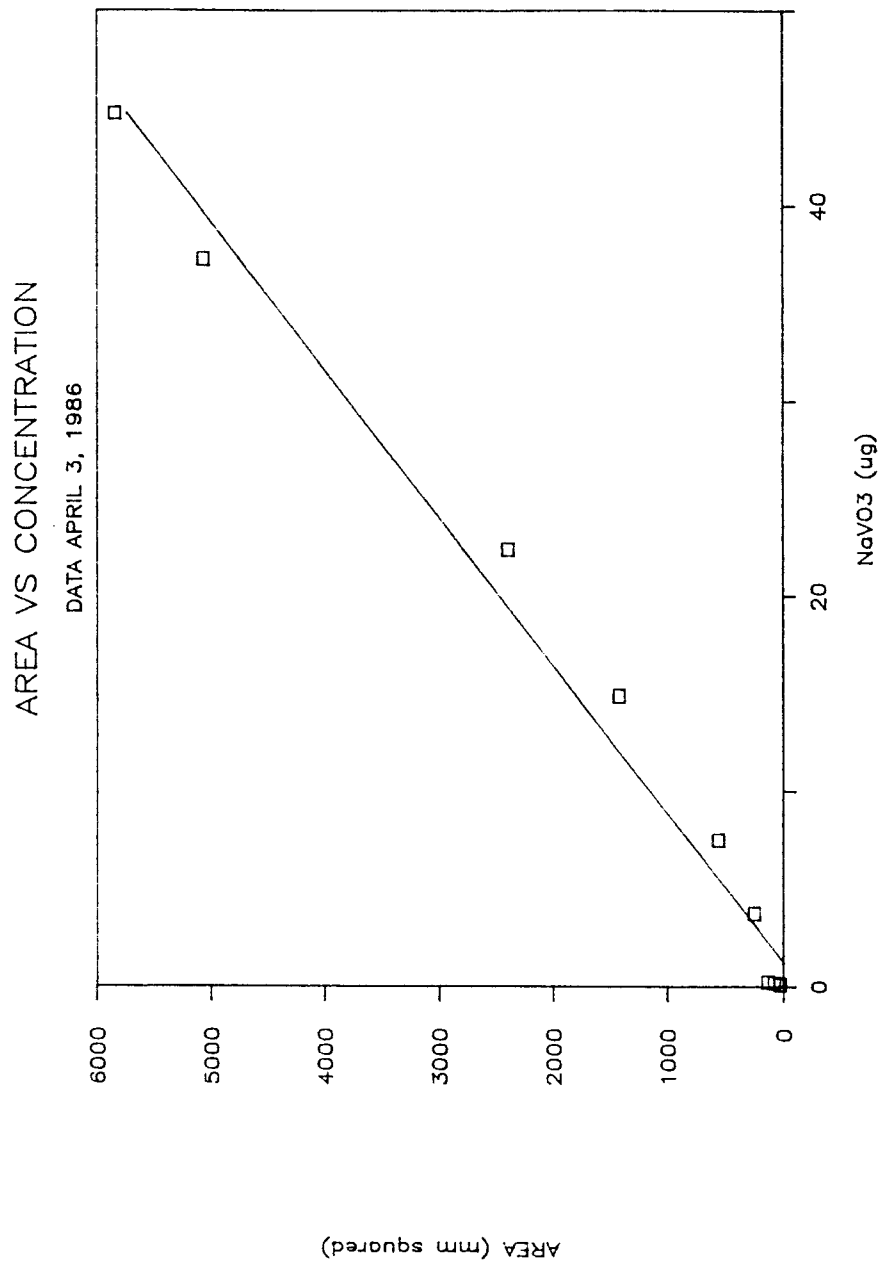

AREA VS CONCENTRATION
DATA APRIL 3, 1986
AREA (mm squared)
NaVO3 (ug)
0
1000
2000
3000
4000
5000
6000
0
20
40

Figure 3.2.2.6 Linear dynamic range for $Na_2S_2O_3$ by ion exchange polymer based technique.

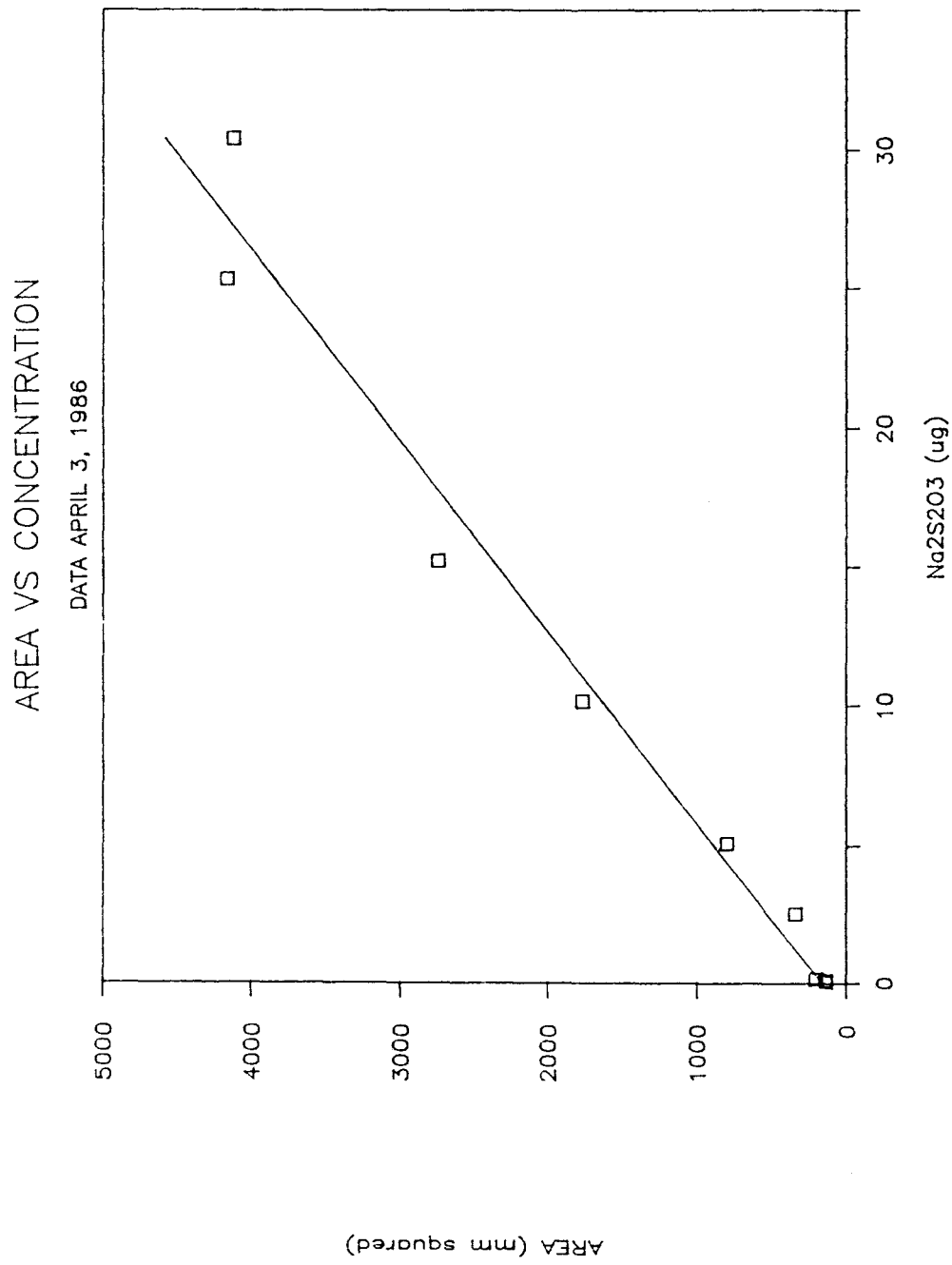

AREA VS CONCENTRATION
DATA APRIL 3, 1986
AREA (mm squared)
5000
4000
3000
2000
1000
0
0
10
20
30
Na2S2O3 (ug)

Figure 3.2.2.7 Linear dynamic range for Na_3Citrate by ion exchange polymer based technique.

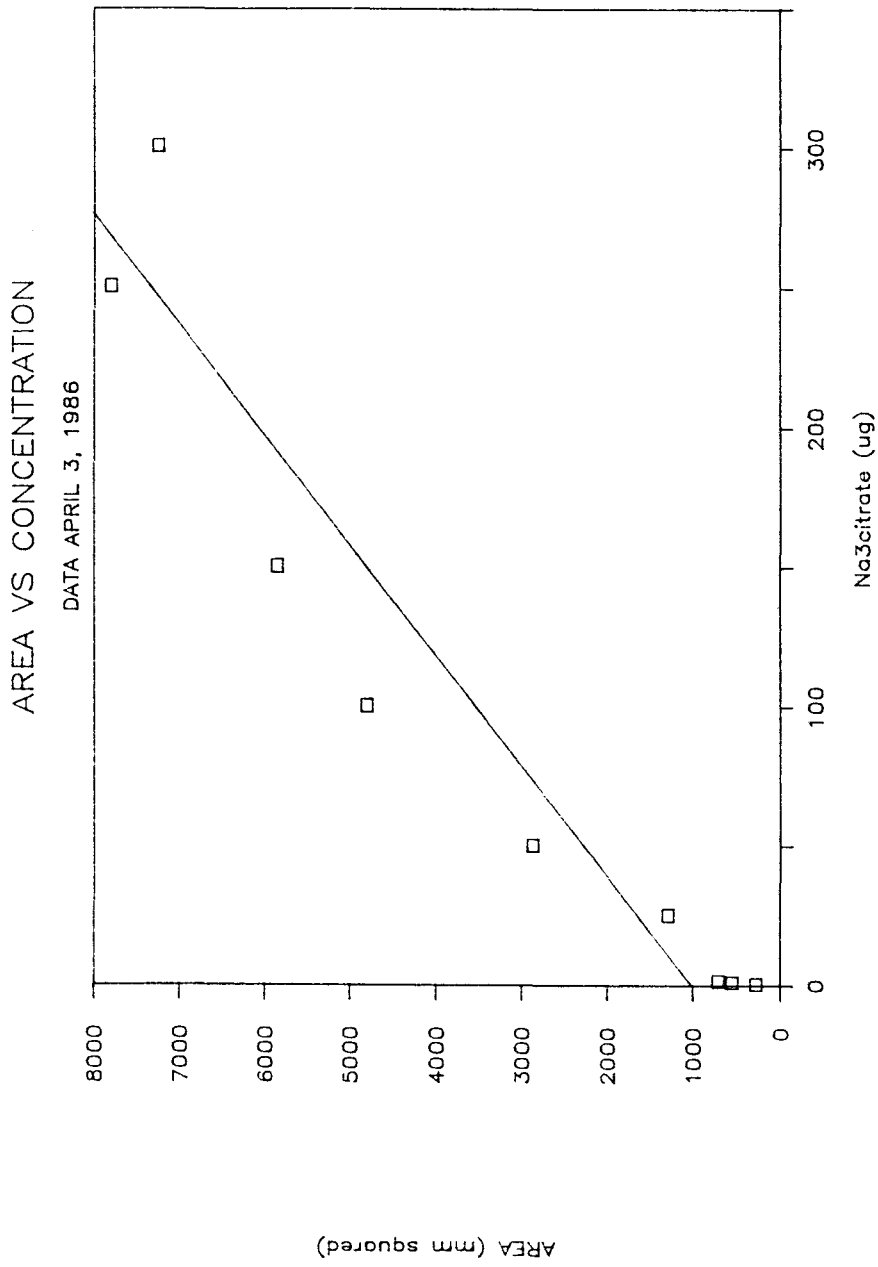

AREA VS CONCENTRATION
DATA APRIL 3, 1986
AREA (mm squared)
Na3citrate (ug)
0
1000
2000
3000
4000
5000
6000
7000
8000
0
100
200
300

Figure 3.2.2.8 Linear dynamic range for NaSCN by ion exchange polymer based technique.

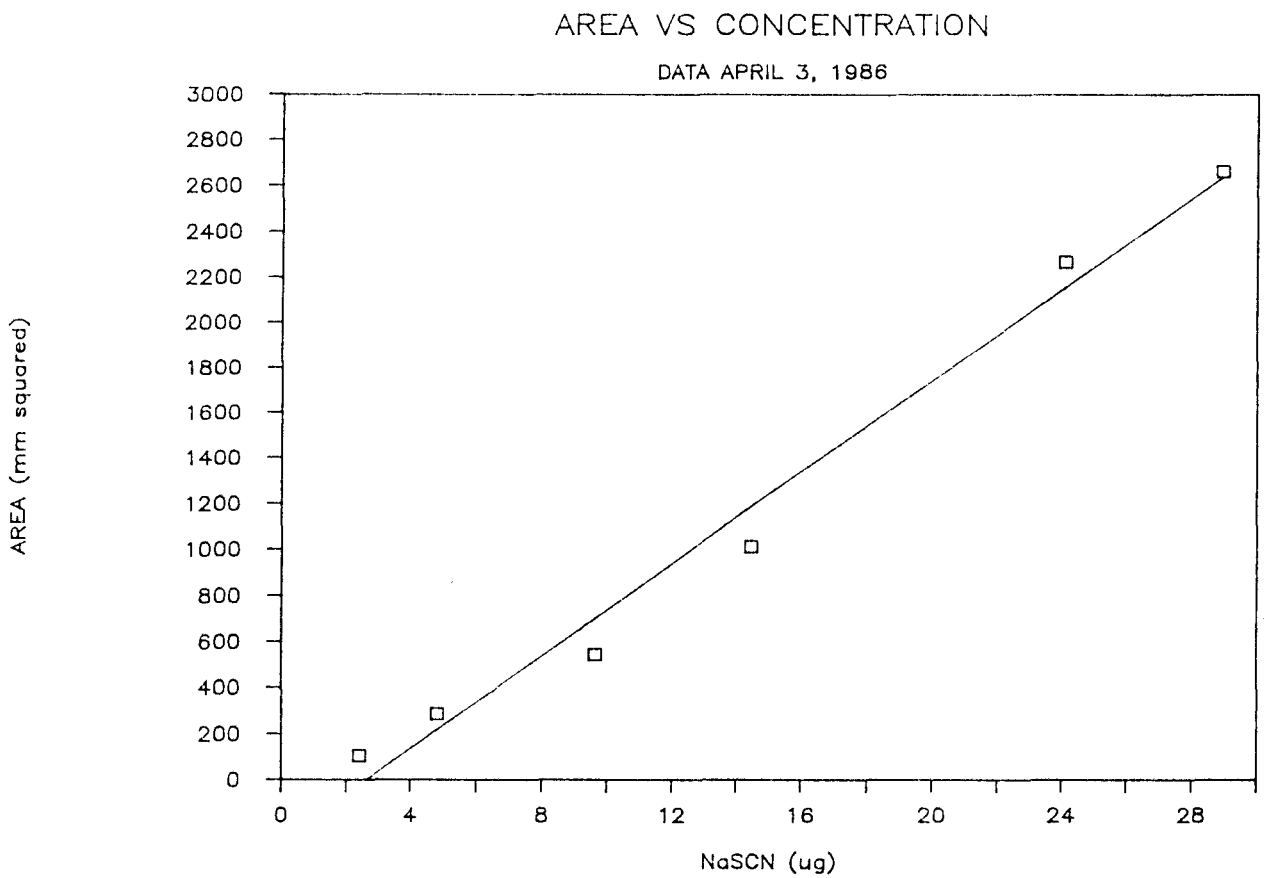

AREA VS CONCENTRATION
DATA APRIL 3, 1986
AREA (mm squared)
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
0
4
8
12
16
20
24
28
NaSCN (ug)

Figure 3.2.2.9 UV/Visible scan of phenol versus H_2O. (concentration 25 mM, pH 10.15)

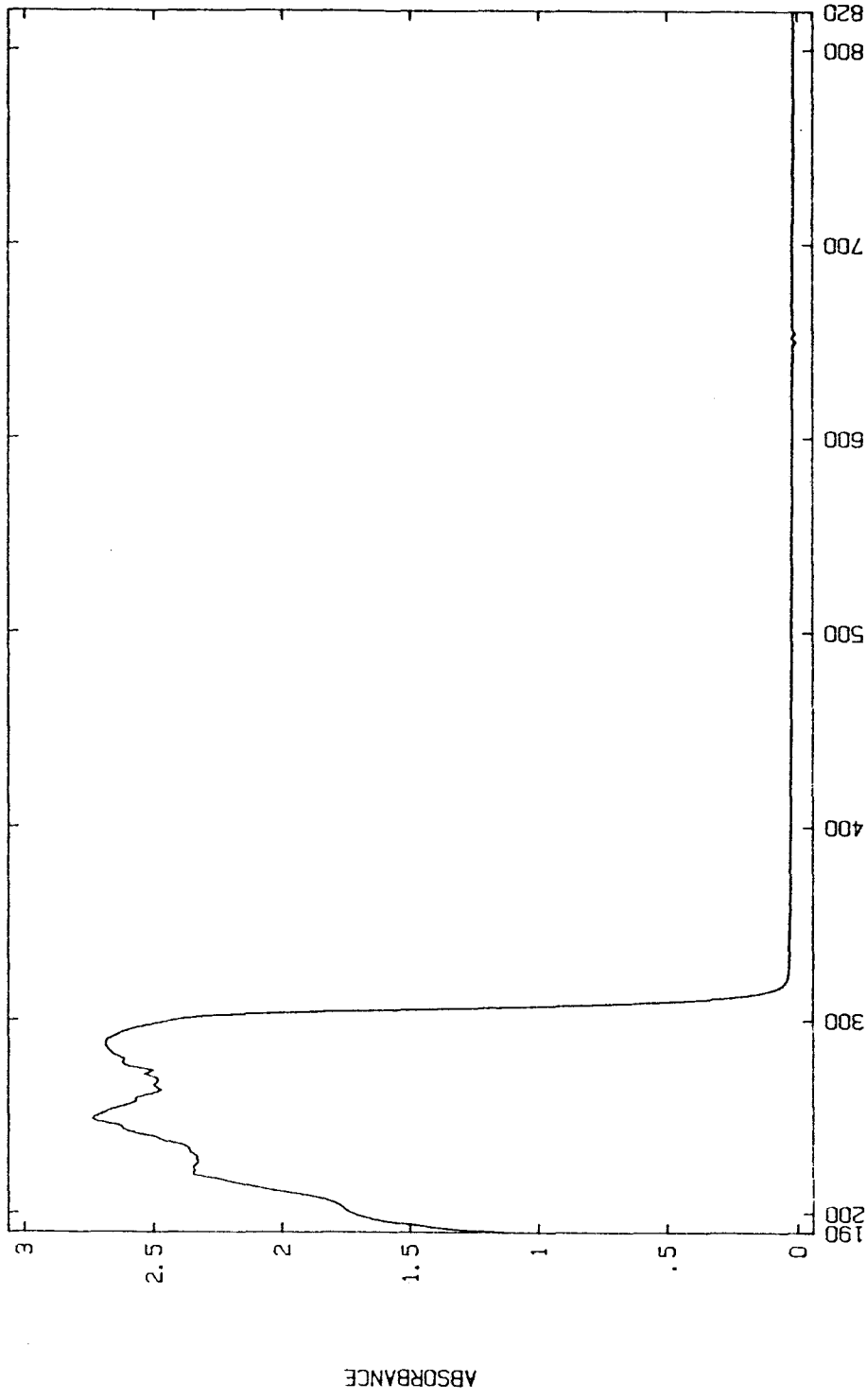

ABSORBANCE
3
2.5
2
1.5
1
.5
0
190
200
300
400
500
600
700
800
820
WAVELENGTH (nm)

Figure 3.2.2.10 UV/Visible scan of Na_2CO_3 versus phenol. (concentration 25 g/L)

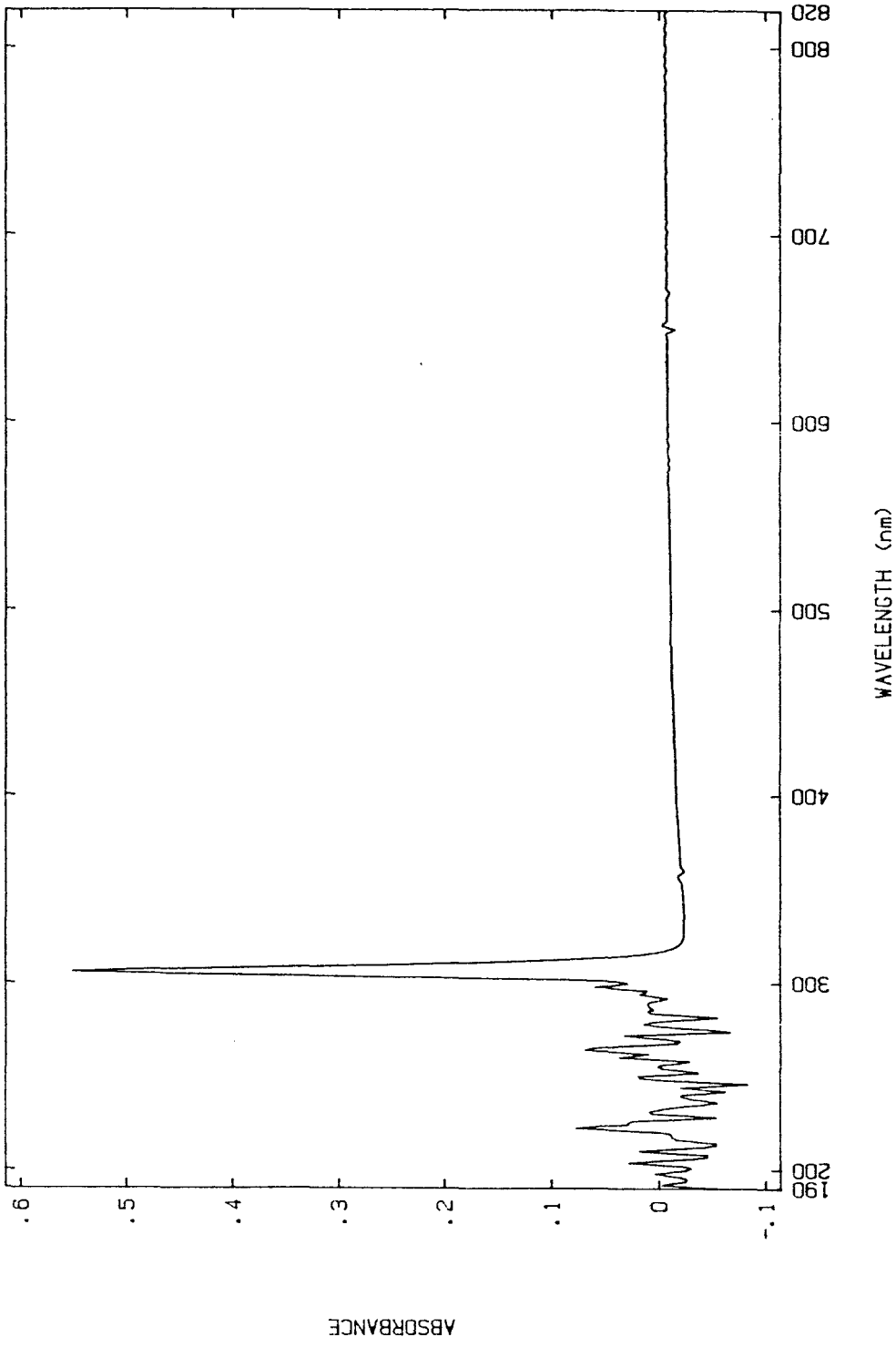

ABSORBANCE
.6
.5
.4
.3
.2
.1
0
-.1
190
200
300
400
500
600
700
800
820
WAVELENGTH (nm)

Figure 3.2.2.11 UV/Visible scan of Na_2SO_4 versus phenol. (concentration 1.2 g/L)

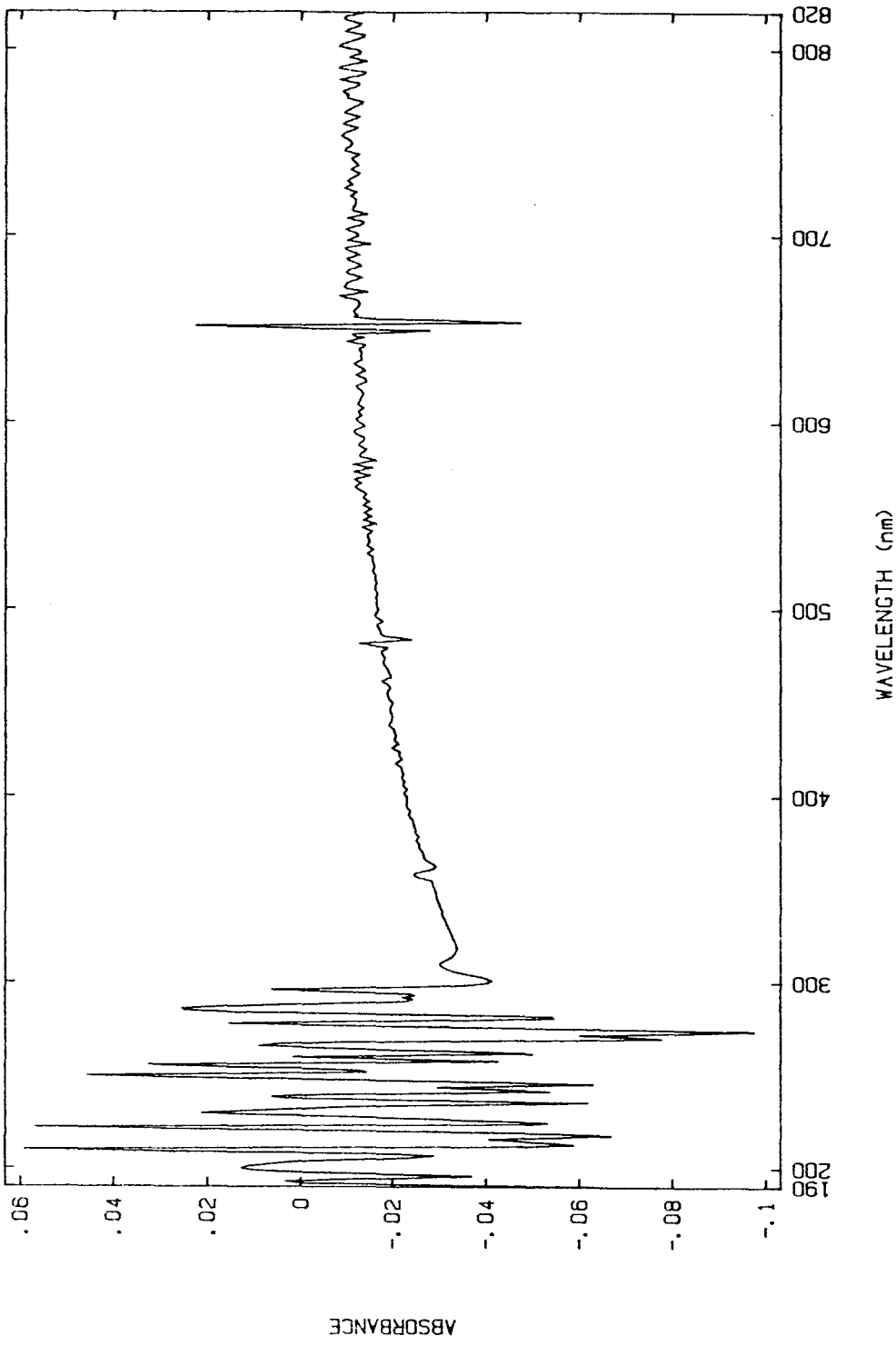

820
800
700
600
500
400
300
200
190
WAVELENGTH (nm)
.06
.04
.02
0
-.02
-.04
-.06
-.08
-.1
ABSORBANCE

Figure 3.2.2.12 UV/Visible scan of $NaVO_3$ versus phenol.
(concentration 1.5 g/L)

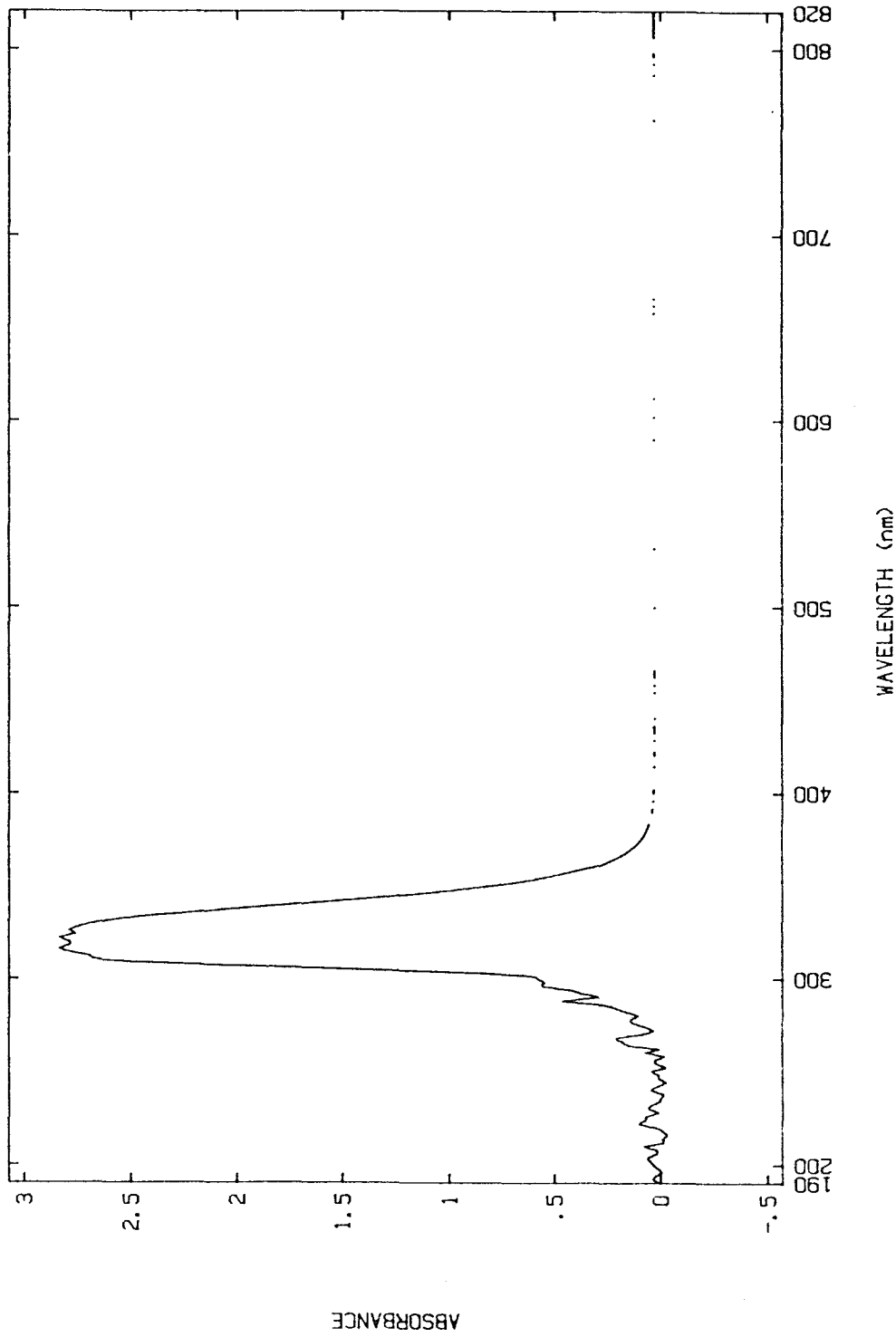

ABSORBANCE
3
2.5
2
1.5
1
.5
0
-.5
190
200
300
400
500
600
700
800
820
WAVELENGTH (nm)

Figure 3.2.2.13 UV/Visible scan of $Na_2S_2O_3$ versus phenol. (concentration 1.4 g/L)

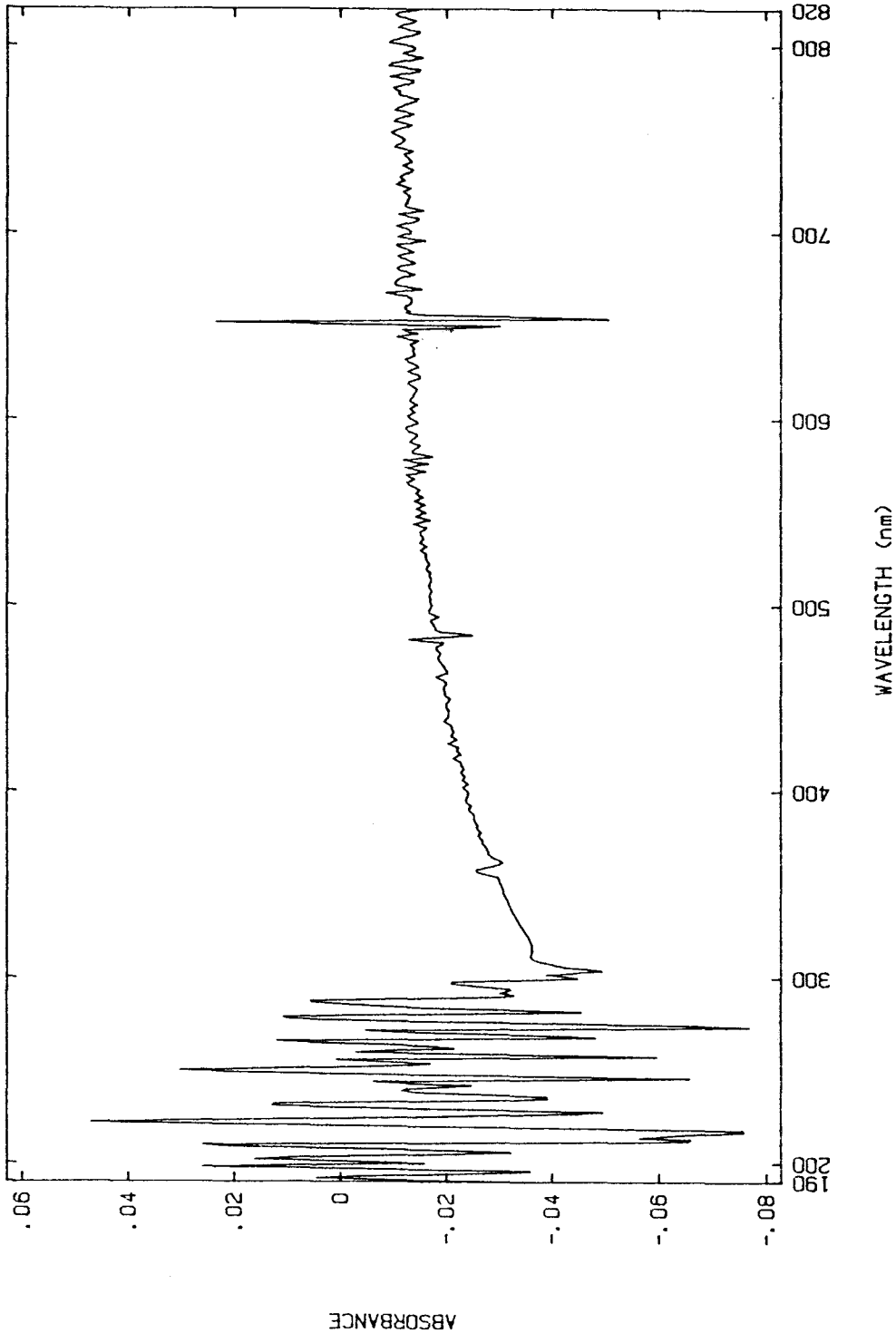

820
800
700
600
500
400
300
200
190
WAVELENGTH (nm)
.06
.04
.02
0
-.02
-.04
-.06
-.08
ABSORBANCE

Figure 3.2.2.14 UV/Visible scan of Na_3Citrate versus phenol. (concentration 10 g/L)

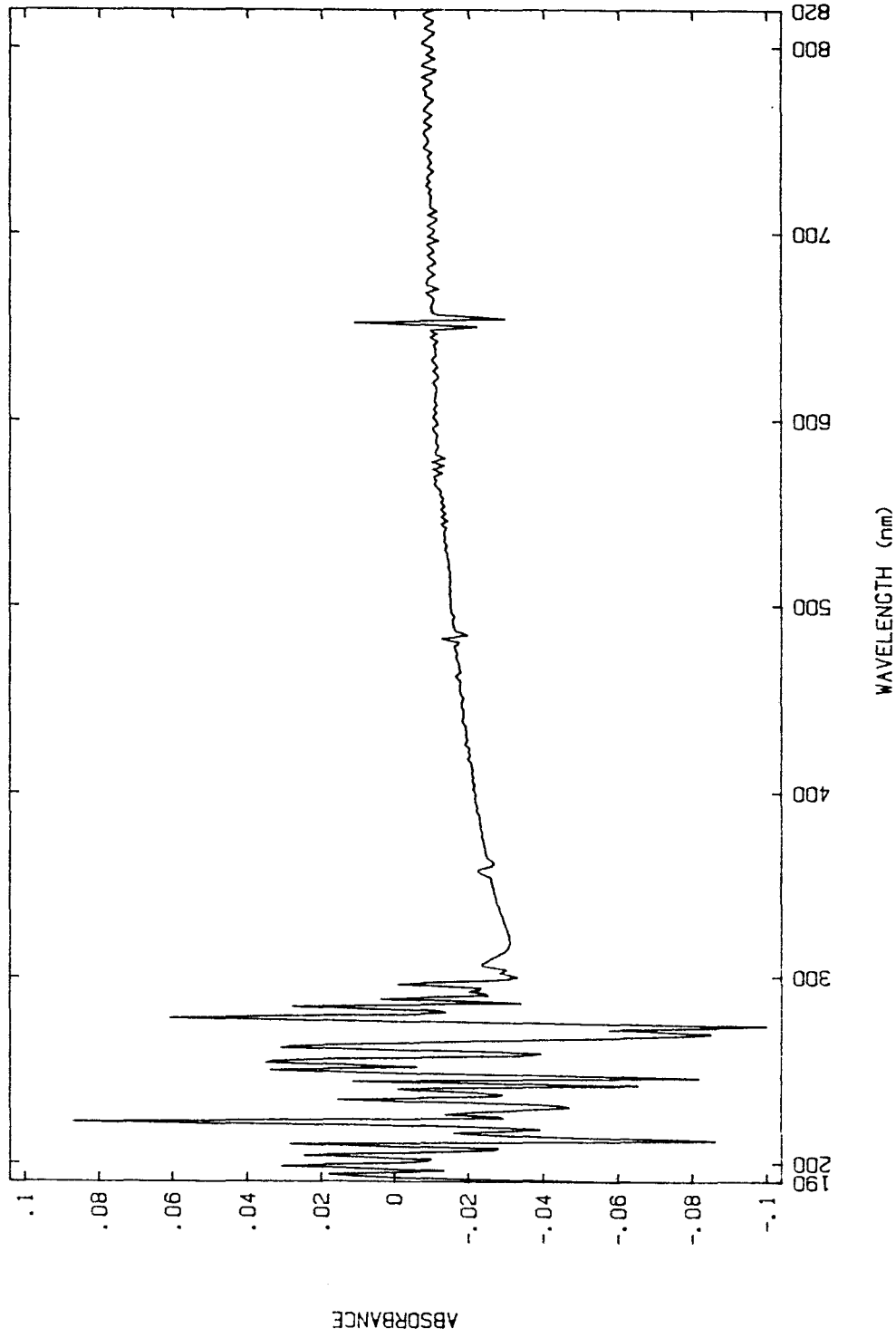

ABSORBANCE
.1
.08
.06
.04
.02
0
-.02
-.04
-.06
-.08
-.1
190
200
300
400
500
600
700
800
820
WAVELENGTH (nm)

Figure 3.2.2.15 UV/Visible scan of NaSCN versus phenol.
(concentration 1.5 g/L)

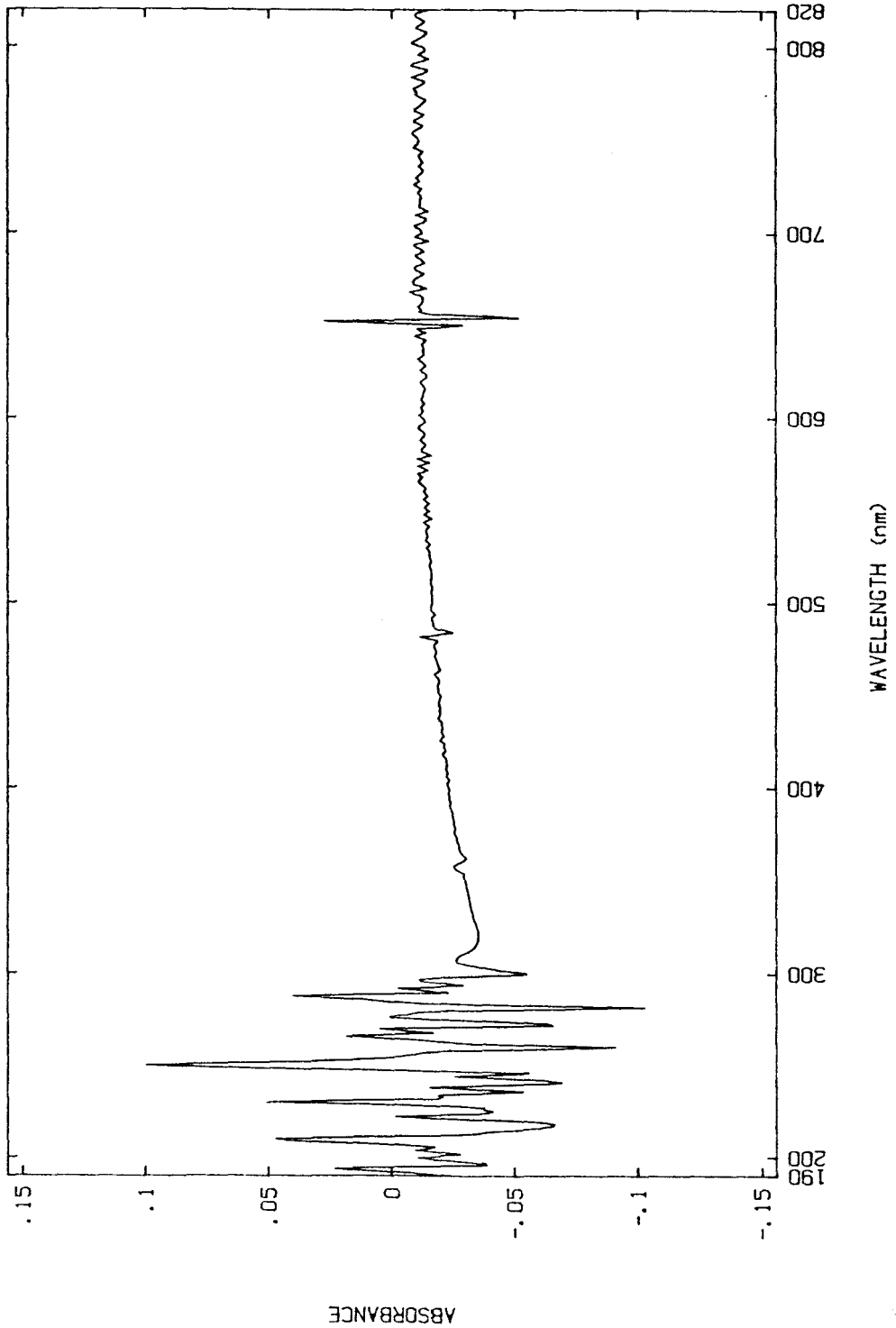
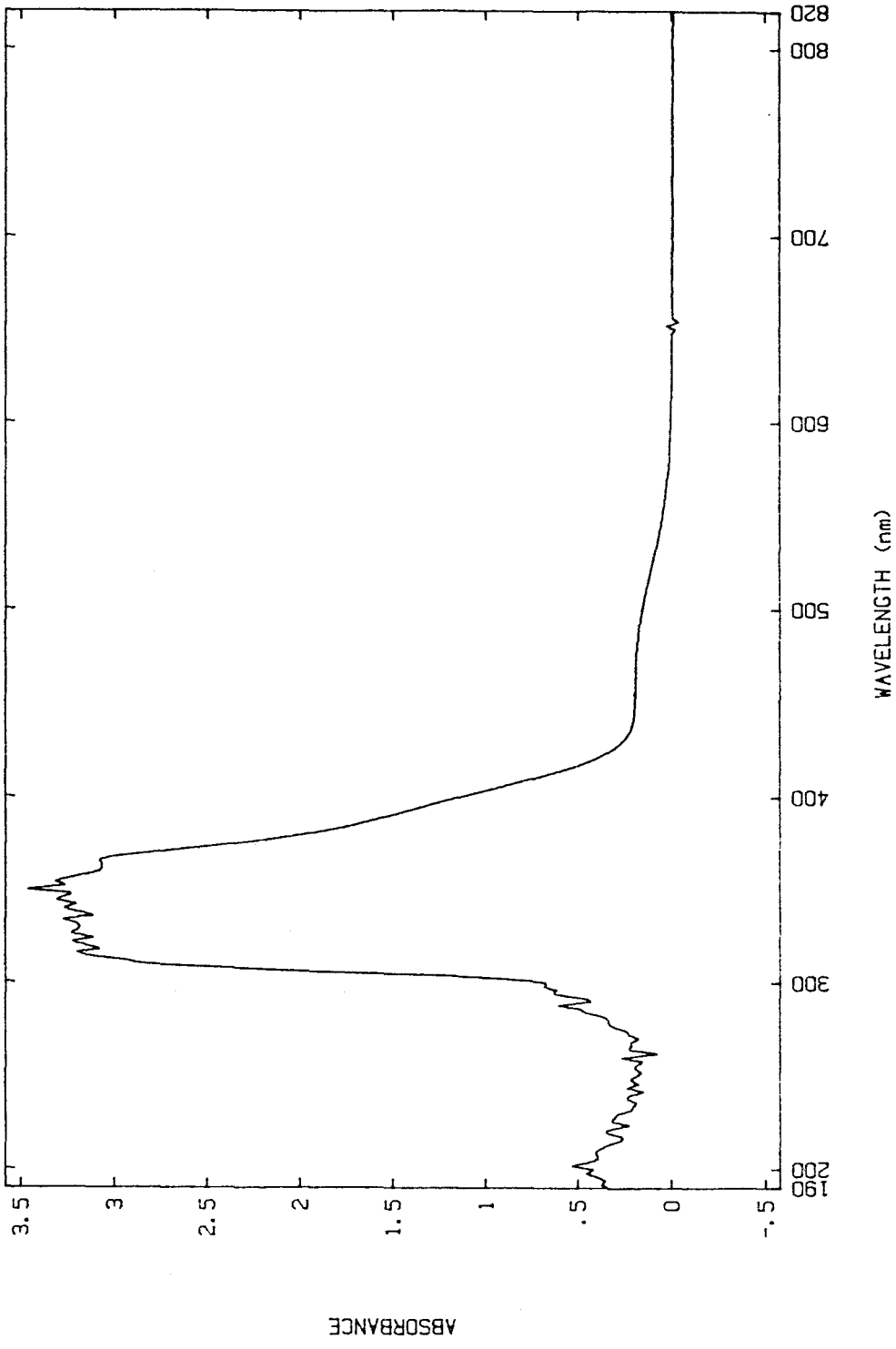

820
800
700
600
500
400
300
200
190
WAVELENGTH (nm)
.15
.1
.05
0
-.05
-.1
-.15
ABSORBANCE

Figure 3.2.2.16 UV/Visible scan of ADA versus phenol.
(concentration 3.0 g/L)


ABSORBANCE
3.5
3
2.5
2
1.5
1
.5
0
-.5
190
200
300
400
500
600
700
800
820
WAVELENGTH (nm)

CHAPTER 4

SUMMARY AND FUTURE WORK

SUMMARY AND FUTURE WORK

4.1 Summary

In summary there are three non-suppressed HPLC routes that can be taken to analyze circulating Stretford liquors; namely ion pair chromatography, silica based ion exchange chromatography and polymer based ion exchange chromatography.

The accuracy of the quantitative results obtained is limited, in part, by the ability of the method to resolve the species involved. The accuracy is further limited by the precision of the methods involved. Similarities are noted when comparing the three methods. One similarity is that the retention times of the anions eluted occur over a reasonable period of time (ie. less than fifteen minutes). Differences do exist among the methods. When comparing resolution, the poorest method is the ion pair method. Inherently, the ion pair method is the poorest method in the repeatability of the analytical results.

Ion pair chromatography does have some merit. Five species can be detected; namely SCN^-, SO_4^{2-}, $S_2O_3^{2-}$, HCO_3^- and S^{2-} when in a mixture. Once again, the resolution is poor. This is particularly true for the pairs of ions noted; $S_2O_3^{2-}/HCO_3^-$ and $S_2O_3^{2-}/SCN^-$. Other limitations of

this method was that there was a poor choice of the internal standard since one did not have full control over the $NaHCO_3$ concentration. Sample preparation (ie. evaporation) involved too much handling. This increased the possibility of contamination as well as the possibility that different sulfoxy anions would be generated.

The silica based ion exchange method proved to be a much better method than the ion pair method with respect to quantification of the by-product anions. Advantages of this method were that the species were very well resolved, a wide linear dynamic range was obtained and the accuracy and precision was better than $\pm$ 10% for the anions. A major drawback to this method was that one could resolve only the by-products of the circulating Stretford liquors. The greatest disadvantage was that by lowering the pH of the solution one could easily cause the sulfoxy anions of the by-products to change form into other sulfoxy anions.

The preferred method is the polymer based ion exchange method. This method has many advantages. It is able to quantify six of eight of the components of the circulating Stretford liquors (except for ADA and polysulfides) to an accuracy better than $\pm$ 10% for the major components. The resolution, of course, is more than adequate to allow such accuracy. Either of two quantitative

techniques; namely standard addition or the calibration curve technique may be used and each gives similar results. There is a wide linear dynamic range for all of the species quantified. There is little sample preparation involved and, since one does not lower the pH of the solution, a change in the form of the sulfoxy anions is unlikely to occur. Once again dilution factors are a limitation since sample anions are present at different levels.

Thus, when comparing the methods, the method that has the best repeatability, retention time, resolution and peak shape is clearly the polymer based ion exchange method.

4.2. Suggestions for Future Work

Since ADA did not elute off of the ion exchange columns, it is proposed that it had strong coulombic interactions with the anion exchange sites. Thus, ion chromatography was not a suitable technique for the analysis of the ADA.

Future work should concentrate on the use of ion pair chromatography for the analysis of this component of the circulating liquors. Reeve has shown that ion pair chromatography can be used on the liquors for the analysis of ADA. Pitts has also shown that it is a good technique to use on pure ADA samples. By perhaps using an ODS column and

different ion pair reagents, success might be encountered in the routine analysis of ADA in the circulating liquors.

A study to better understand the ion exchange and the ion pair mechanisms as related to the separation should also be undertaken.

REFERENCES

REFERENCES

1. Analytical Methods for the Holmes Stretford Process, Peabody Holmes Ltd., Turnbridge, England, p.18.
2. M.A.H. Habayeb, PhD Thesis, Department of Chemistry, McMaster University, Hamilton, Ontario (1981) p.83, 96.
3. A. Albert, E.P. Serjeant, The Determination of Ionization Constants, Chapman and Hall, New York (1984) pp.162-3.
4. Analytical Methods for the Holmes Stretford Process, Peabody Holmes Ltd., Turnbridge, England, p.20.
5. H. Auterhoff, and I. Schwingel, Arch. Pharm., 308, #8 (1975) pp.583-587.
6. Analytical Methods for the Holmes Stretford Process, Peabody Holmes Ltd., Turnbridge, England, p.10.
7. Analytical Methods for the Holmes Stretford Process, op. cit., p.19.
8. Analysis of Stretford Solutions for Vanadium, Method 10.7, Appendix 3, Stretford Process Design Manual, British Gas Corp.(1971) pp.21-22.
9. B.Thornton, M.Sc. Thesis, Department of Chemistry, McMaster University, Hamilton, Ontario (1972) p.41-44.
10. S.A. Shcherbakova, N.V. Mel'chakova, and V.M. Peskkova, J.Anal. Chem. of USSR, 31 (1976) pp.271-273.

11. Analytical Methods for the Holmes Stretford Process, op. cit., p.19.

12. W. Giggenbach, Inorg. Chem., 11, #6 (1972) pp.1201-1207.

13. Analytical Methods for the Holmes Stretford Process, op. cit., p.22.

14. Analytical Methods for the Holmes Stretford Process, op. cit., Appendix 2.

15. Analytical Methods for the Holmes Stretford Process, op. cit., p.23.

16. Analytical Methods for the Holmes Stretford Process, op. cit., p.25.

17. K. Cunningham, M.C. Goldberg, E.R. Weiner, Anal. Chem., 49, #1 (1977) pp.70-75.

18. Analytical Methods for the Holmes Stretford Process, op. cit., pp.21-22.

19. M.T.W. Hearn, Advances in Chromatography, 18 (1980) pp.59-100.

20. R.N. Reeve, J. Chromatog., 177 (1979) pp.393-397.

21. The Analysis of ADA Isomers In Commercial Products and Stretford Solutions by HPLC, Union Oil, P.O. Box 76, Brea, CA, (1985).

22. Isomeric Distribution of 'ELVADA' by HPLC, North West Gas, Scientific Services Department, September 19,1985.

23. T. Sunden, M. Lindgren, A. Cedergren and D.D. Siemers, Anal. Chem., 55 (1983) pp.2-4.

24. P.R. Haddad and A.L. Heckenberg, J. Chromatog., 300 (1984) pp.357-394.

25. D.T. Gjerde, J.S. Fritz and G. Schmuckler, J. Chromatog., 186 (1979) pp.509-519.

26. S. Dogan and W. Haerdi, Chimia, 35, #9 (1981) pp.339-342.

27. K.J. Stetzenbach and G.M. Thompson, Ground Water, 21, #1 (1983) pp.36-41.

28. R.A. Cochrane and D.E. Hillman, J. Chromatog., 241 (1982) pp.392-394.

29. R.H. Mistry, "Progress Report on HPLC Investigations to December 1977: Ion-exchange Investigations." Peabody Holmes Ltd., Report RDD 1343, September 1978.

30. J.R. Benson and D.J. Woo, J. Chromatog. Sci., 22 (1984) pp.386-399.

31. T. Sunden, M. Lindgren, A. Cedergren and D.D. Siemers, Anal. Chem., 55 (1983) pp.2-4.

32. T. Okada, and T. Kuwamoto, Anal. Chem., 55 (1983) pp.1001-1004.

33. J.S. Fritz, D.L. DuVal and R.E. Barron, Anal. Chem., 56 (1984) pp.1177-1182.

34. Hamilton Company, Bulletin for PRP-X100, Reno, NV., 1985.

35. Waters Scientific, Ion Chromatography Bulletin, Milford, MA, 1985.

36. S.J. Pitts, M.Sc. Thesis, Department of Chemistry, McMaster University, Hamilton, Ontario (1983) pp.33-36.

37. K.J. Stetzenbach and G.M. Thompson, op. cit., pp.36-41.

38. L.R. Snyder and J.J. Kirkland, Introduction to Modern Liquid Chromatography, John Wiley and Sons Inc., Toronto (1979) pp.454-457.

39. L.R. Snyder and J.J. Kirkland, op. cit., pp.458-470.

40. L.R. Snyder and J.J. Kirkland, op. cit., pp.454.

41. L.R. Snyder and J.J. Kirkland, op. cit., pp.419-423.

42. L.R. Snyder and J.J. Kirkland, op. cit., pp.414-418.

43. L.R. Snyder and J.J. Kirkland, op. cit., pp.424-426.

44. F.C. Smith and R.C. Chang, The Practice of Ion Chromatography, John Wiley and Sons Inc., Toronto (1983) p.202.

45. G.E.P. Box, W.G. Hunter and J.S. Hunter, Statistics for Experimenters, John Wiley and Sons Inc., Toronto (1978) pp.170-175.

46. A.W. Wolkoff, R. H. Larose, Analytical Chemistry, 47, #7 (1975) pp.1003-1008.

APPENDICES

APPENDIX 1

A.1 ANOVA Evaluation

This appendix contains the necessary equations in order to perform a regression analysis and test the parameters in the resulting linear model.

A.1 ANOVA Evaluation

In order to perform an analysis of variance the least squares regression line must first be evaluated. The line $y=\beta_0 + \beta_1 x$ is calculated where β_0 is the y intercept and β_1 is the slope of the least squares line.

This line is best calculated through the evaluation of the matrix:

$$\begin{bmatrix} \Sigma x_{1u}^2 & \Sigma x_{1u}x_{2u} \\ \Sigma x_{1u}x_{2u} & \Sigma x_{2u} \end{bmatrix} \begin{bmatrix} \beta_0 \\ \beta_1 \end{bmatrix} = \begin{bmatrix} \Sigma x_{1u}y_{1u} \\ \Sigma x_{2u}y_{2u} \end{bmatrix}$$

where x_{1u} and x_{2u} are the sample masses and y_{1u} and y_{2u} are the sample areas. Through evaluation of this matrix β_0 and β_1 can be determined.

In order to determine the significance of the model β_1 is evaluated to determine if the straight line model is applicable. The total sum of squares for the model is determined through the calculation of the sum of squares of the areas which is represented by Σy^2, a correction factor accounting for the difference from the mean is then subtracted. This correction factor is calculated by $((\Sigma y)^2/n)$ where n is the number of data points. The total sum of squares corrected for the mean (CFM) is then calculated by subtraction of the correction factor (C.F.) from the crude sum of squares. That remaining accounts for the error terms.

The error can be divided into two terms that due to regression and that due to the residuals. The residual sum of squares is calculated by subtraction of the best fit area from the area $\Sigma(y-\hat{y})^2$. The regression accounts for the difference between the total(CFM) and the residuals. The degrees of freedom (df) for the regression is calculated from the number of parameters subtract one and for the residuals by the number of data points subtract the number of parameters.

The mean square (MS) for the residuals is calculated by the sum of its squares divided by the degrees of freedom for the residuals. Likewise, the mean square for the regression is calculated by the sum of its squares divided by its degrees of freedom.

The hypothesis of H_0: MS(Residual)=MS(Regression) is tested against H_1: MS(Residual)>MS(Regression). The ratio of these two is commonly called an F distribution where the null hypothesis is rejected for $F>F_{\alpha}(\nu 1 \cdot \nu 2)$, where α=0.05, the level of significance and ν1 is the degrees of freedom for the regression and ν2 is the degrees of freedom for the residuals.

APPENDIX 2

A.2 Standard Addition

This appendix contains the necessary equations in order to perform standard addition analysis.

A.2 Standard Addition

The standard addition technique will allow one to determine the concentration of the analyte with respect to itself. To perform the standard addition method, the analyte itself is added in a known level to the sample. Two analysis are necessary, both before and after spiking.

The assumptions of identical injection volumes and negligible change upon spiking can be made. The concentration of the sample anion can then be evaluated through the following equation:

$$C_X = \frac{W_S}{V} \frac{1}{(A'_{XS}/A_X) - 1}$$

where C_X is the concentration of the sample anion (in g/L)

W_S is the mass of the spike (in mg)

V is the volume of the sample (in mL)

A'_{XS} is the area of the peak after spiking (in mm^2)

A_X is the area of the peak prior to spiking (in mm^2)

Note that the area of the peak is calculated from the product of the peak height and the width of the peak at half the peak height.