STUDIES ON VANADIUM ANALYSES OF STRETFORD LIQUORS

To

my parents

They gave me the opportunity.

STUDIES ON
VANADIUM ANALYSES OF STRETFORD LIQUORS

By

BARRY KENNETH THORNTON A.I.T. (W.A.)

A Thesis
Submitted to the Faculty of Graduate Studies
in Partial Fulfilment of the Requirements
for the Degree
Master of Science

McMaster University
August 1972

MASTER OF SCIENCE (1972)
(Chemistry)

McMASTER UNIVERSITY
Hamilton, Ontario

TITLE: Studies on Vanadium Analyses of Stretford Liquors

AUTHOR: Barry Kenneth Thornton A.I.T. (W.A.) Western Australian Institute of Technology

SUPERVISOR: Dr. O. E. Hileman, Jr.

NUMBER OF PAGES: ix, 66

SCOPE AND CONTENTS:

A brief review of the industrial methods employed to remove hydrogen sulfide from contaminated gas streams is given, with particular emphasis centred on the Stretford process.

A summary of some recent developments in the solvent extraction of vanadium(5) is also given, together with the relevant aqueous vanadium chemistry.

The experimental section deals with the development and optimization of an analytical procedure for vanadium(5) determination in alkaline solution. This developed procedure is then applied to the analysis of Stretford liquor.

ACKNOWLEDGEMENTS

I would like to thank Dr. O. E. Hileman, Jr., for his advice and enthusiasm throughout the course of this research, and for allowing me to leave without ever beating him at handball.

I should also like to thank the fellow members of our research group, not for stimulating discussions, but for their friendship.

Financial assistance by the province of Ontario and McMaster University is gratefully acknowledged.

Finally I am especially grateful to my wife, Rosemary, for her warmth and understanding over the past two years.

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I. INTRODUCTION

I.A. Statement of the Problem

Routine chemical analysis of industrial plant liquors on a daily basis is often not possible due to the complex nature of these liquors. Industrial liquors often vary in composition from day to day, and analysis for any individual species present in solution may be intractable due to changing interferences. This is true in the case of the Stretford plant liquor where routine chemical analysis for total vanadium is possible, but analysis for either vanadium (4) or (5) is not. It is therefore the aim of this thesis to develop a method of analysis for vanadium (5) that could then be applied to the Stretford liquor.

I.B. Development of the Stretford Process

Man is not entirely responsible for air pollution, occasionally nature itself is guilty. Consider, for example, the large quantities of ash, dust and hydrogen sulfide spewed into the atmosphere by volcanic erruption or the pollution caused when the tiny island of Krakatoa exploded in 1833. Millions of cubic feet of gas were released into the atmosphere and fly ash was observed for months after the explosion. Lately, however, man has taken up the challenge and has succeeded in developing thousands of new methods of polluting the air.

One of the biggest air pollution sources results from the industrial process of cokeing coal(4). This produced gas is often associated with quantities of hydrogen sulfide (0.3 - 3%), hydrogen cyanide (0.1 - 0.25%) and ammonia (1.1%). All of these gases are undesirable in the atmosphere, but we will restrict ourselves to only one of these: hydrogen sulfide.

Hydrogen sulfide can be detected by the sense of smell at a concentration of 0.2 ppm. It is a colorless, flamable gas with an offensive odour. It is both an irritant and an asphyxiant. At low concentrations, 10 ppm to 150 ppm, it causes irritation of the eyes and respiratory tract. At higher concentrations it has a great effect on the central nervous system. Exposure to concentrations of 500 ppm for approximately 30 min causes dizziness and headache, while exposure to concentrations greater than 800 ppm can prove instantaneously fatal(1,2,3).

For the above reasons industry has strived to find an effective and economical method of scrubbing hydrogen sulfide from gas streams before discharging them into the atmosphere, with the aim of minimizing atmospheric pollution.

One of the first methods developed was the so-called "oxide box" method. This consisted of passing the contaminated gas over beds of finely divided iron oxide (see Fig. 1). The oxide was initially supported on sawdust, or crushed slag and later in towers (see Fig. 2). The mechanism of conversion requires two steps. Firstly, the conversion of the iron oxide to iron sulfide and then the subsequent reoxidation of the iron sulfide to iron oxide with the production of sulfur.

$$3H_2S + Fe_2O_3 \longrightarrow Fe_2S_3 + 3H_2O \qquad [1]$$

$$2Fe_2S_3 + 3O_2 \longrightarrow 2Fe_2O_3 + 6S \qquad [2]$$

$$\text{net equation:}\quad 2H_2S + O_2 \longrightarrow 2H_2O + 2S \qquad [3]$$

This process is enhanced if the gas stream is enriched with oxygen and if the temperature of reaction is kept at 100°F(4,5). The sulfur which is deposited on the iron oxide may be reclaimed by solvent extraction with

Fig. 1. "Iron Box" Process Flow Chart.

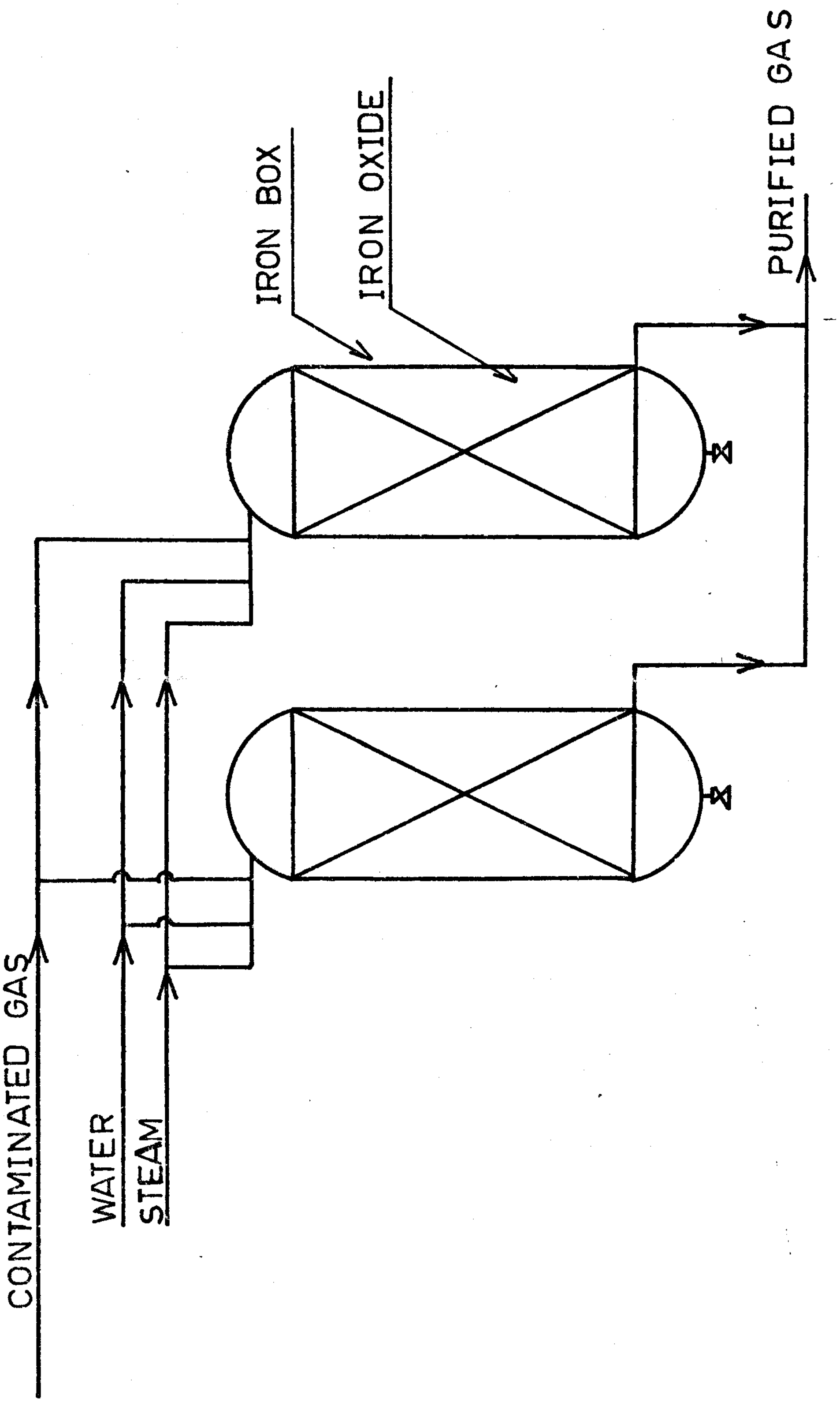
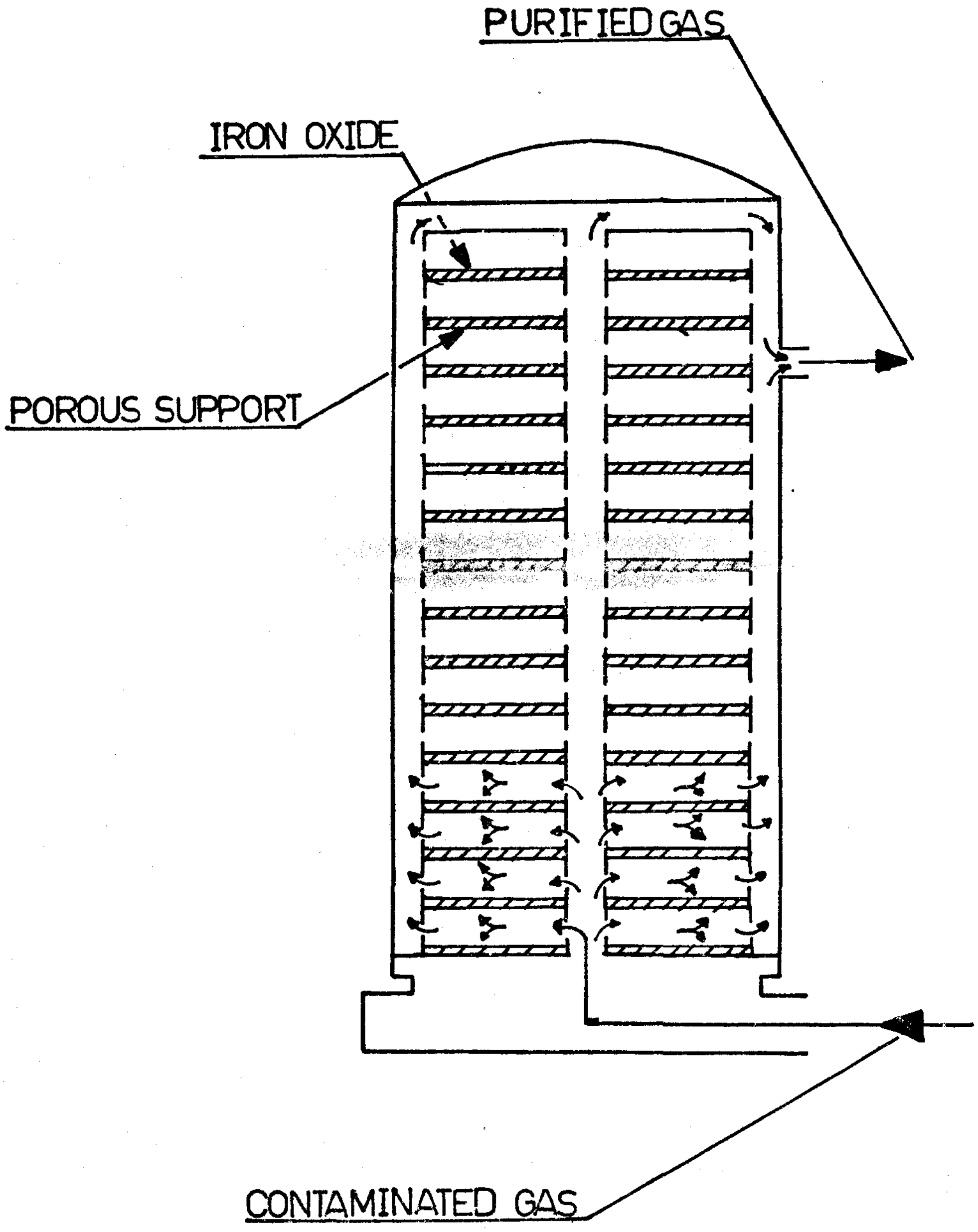

CONTAMINATED GAS
WATER
STEAM
IRON BOX
IRON OXIDE
PURIFIED GAS

Fig. 2. Support Tower For Iron Oxide In The "Iron Box" Process.


PURIFIED GAS
IRON OXIDE
POROUS SUPPORT
CONTAMINATED GAS

carbon disulfide. Usually, however, it is uneconomical to attempt to recover the sulfur, and it is common to dispose of the iron oxide/sulfur granuals for fertilizer.

The iron box method of gas purification has problems associated with it, not the least of which was the opposition of organized labor groups to the task of cleaning the boxes. The job was one of the dirtiest and most disliked in industry.

Since hydrogen sulfide is frequently associated with hydrogen cyanide and hydrogen cyanide reacts irreversibly with iron oxide according to the equation [4], the iron oxide eventually becomes poisoned and must be replaced.

$$6HCN + Fe_2O_3 \longrightarrow Fe_2CN_6 + 3H_2O \qquad [4]$$

This is just one more limitation of the iron box method.

It was evident to early workers in the gas purification field that the "iron box" method was unworkable if large volumes of gas were to be purified or if the gas was contaminated with hydrogen cyanide. The early developments in gas purification turned away from "dry" methods of gas cleaning towards the "wet" methods. Basically these consisted of: adsorption of the gas into a suitable media, conversion of the hydrogen sulfide to sulfur by some agent present in solution, then regeneration of the adsorbing solution.

One such wet process is the "Manchester process", where the adsorbing media is a sodium carbonate solution and the converting agent is iron oxide. The basic chemistry is shown below.

$$H_2S + Na_2CO_3 \longrightarrow NaHS + NaHCO_3 \qquad [5]$$

$$Fe_2O_3 \cdot 3H_2O + 3NaHS + 3NaHCO_3 \longrightarrow Fe_2S_3 \cdot 3H_2O + 3Na_2CO_3 + 3H_2O \qquad [6]$$

$$2Fe_2S_3 \cdot 3H_2O + 3O_2 \longrightarrow 3Fe_2O_3 \cdot 3H_2O + 6S \qquad [7]$$

$$\text{net} \quad 2H_2S + O_2 \longrightarrow 2S + 2H_2O \qquad [8]$$

The Manchester process flow diagram is shown in Fig. 3. This process has the advantage that the converting agent (Fe_2O_3) is continually regenerated, and that the sulfur produced is of very high quality.

The continuing refinement of the Manchester process in England led ultimately to the development of the Stretford process in 1929; this is currently one of the most extensively used industrial gas purification systems. Basically the Stretford process is a wet purification procedure (see Fig. 4) using anthraquinone disulfonic acid instead of iron oxide as the oxidizing agent. The Stretford process also uses sodium carbonate solution as the adsorbent. Anthraquinone disulfonic acid is reduced by the hydrogen sulfide producing sulfur; the hydroquinone disulfonic acid is then reoxidized in the presence of a vanadium catalyst(6,7,8) according to the equations shown below.

$$2OH^- + H_2S + V(5) \longrightarrow H_2O + S\downarrow + V(4) \qquad [9]$$

$$ADA + H_2S \longrightarrow H_2ADA + S\downarrow \qquad [10]$$

$$H_2ADA + O_2 \longrightarrow ADA + H_2O_2 \qquad [11]$$

$$H_2O_2 + V(4) \longrightarrow H_2O + V(5) + 2OH^- \qquad [12]$$

The process can work using only anthraquinone disulfonic acid and no vanadium but the time taken for the reaction in this case is appreciable (20-30 min) and large delay tanks are required.

The Stretford process has the advantage of being able to convert hydrogen sulfide to sulfur on a continuous basis and the sulfur produced is of very high purity. The Stretford process has some limitations, however; the most undesirable of these is the eventual build-up of thiosulfate by the

Fig. 3. "Manchester" Process Flow Chart.

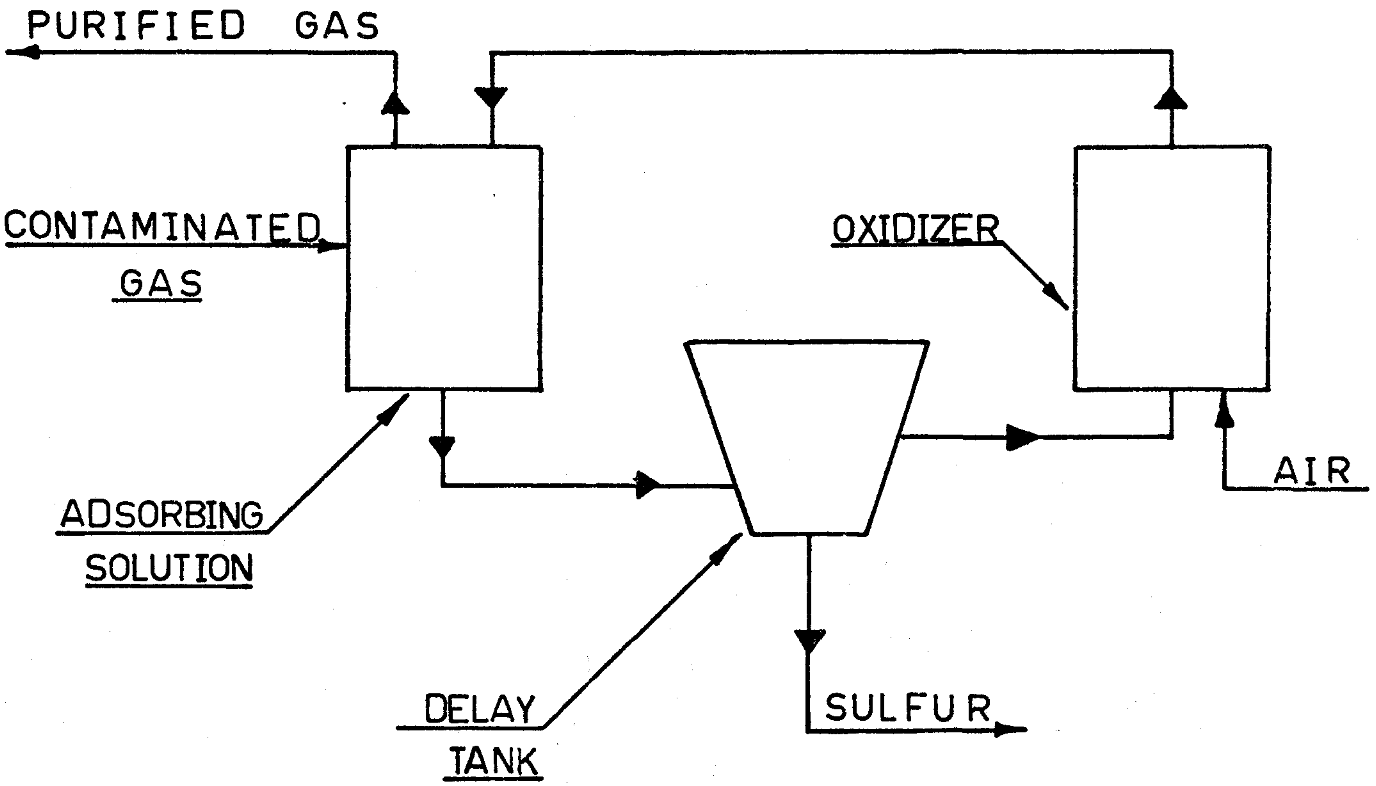
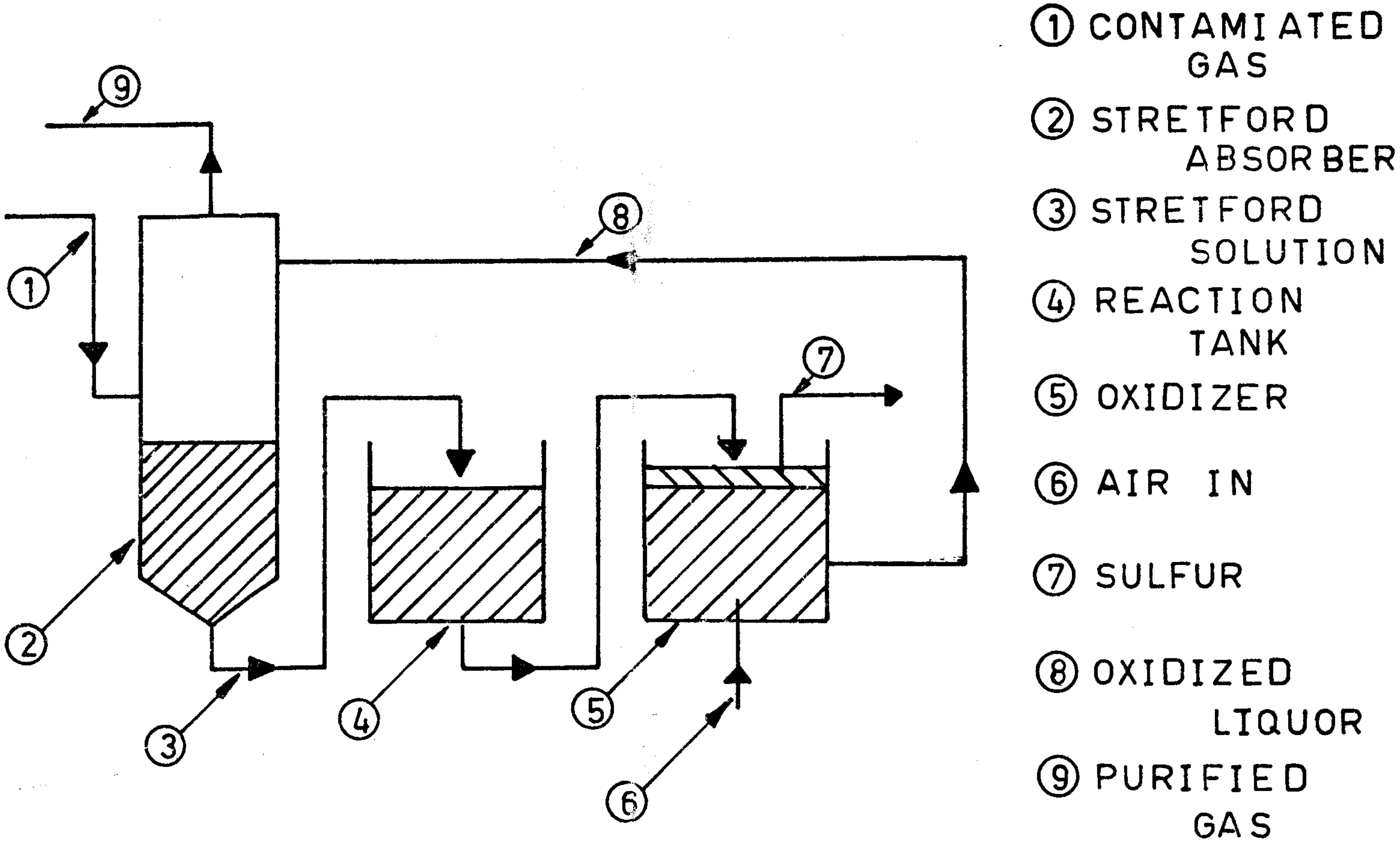

PURIFIED GAS
CONTAMINATED GAS
ADSORBING SOLUTION
OXIDIZER
AIR
DELAY TANK
SULFUR

Fig. 4. "Stretford" Process Flow Chart.


① CONTAMIATED GAS
② STRETFORD ABSORBER
③ STRETFORD SOLUTION
④ REACTION TANK
⑤ OXIDIZER
⑥ AIR IN
⑦ SULFUR
⑧ OXIDIZED LIQUOR
⑨ PURIFIED GAS
①
②
③
④
⑤
⑥
⑦
⑧
⑨

following side reaction.

$$2NaHS + 2O_2 \longrightarrow Na_2S_2O_3 + H_2O \qquad [13]$$

This build-up of thiosulfate continues to a point where the solubility limit is reached, and crystallization occurs. At this point the circulating liquor must be either replaced completely, or in part with fresh liquor. This is the major disadvantage of the process, because disposal of the spent plant liquor is difficult due to the pollution problems associated with vanadium and thiosulfate discharge. The discharge is also expensive because at present no practical method for recovering the vanadium catalyst is available.

The second disadvantage of the Stretford process is that the adsorbing solution (sodium carbonate) is able to adsorb more hydrogen sulfide from the gas stream than the system is immediately capable of oxidizing. At this point, the vanadium precipitates from solution as an insoluble black solid(6). The composition of the solid is variable, and is apparently nonstoichiometric(10). Because of the ease with which the plant may become overloaded with hydrogen sulfide, it is desirable to monitor the vanadium(5)/vanadium(4) ratio present in the Stretford solution at all times. This vanadium(5)/vanadium(4) ratio gives a measure of the ability of the plant to convert further hydrogen sulfide from the gas stream to sulfur. At present it is not possible to determine the vanadium(5)/vanadium(4) ratio, and it was the aim of this thesis to develop a method of analysis for the vanadium(5) concentration in the Stretford liquor.

I.C. Aqueous Vanadium Species

I.C.1. Vanadium(5)

The search for an understanding of the aqueous solution chemistry of vanadium(5) has been with us since Berzelius' work in 1831. It has long been observed that the diffusion rate of vanadium in solution is dependent on pH. This observation alone indicates that the vanadium(5) species present is a function of the pH. The first attempts to clarify this picture were by Jander and Jahr(13). By diffusion studies they were able to postulate that the vanadium(5) species in highly acidic solution was VO_2^+, and in highly alkaline media the vanadium(5) was present as VO_4^{3-}. Their work also suggested that vanadium(5) existed as aggregates in neutral solution. They termed this species a poly-vanadate.

It was not until 1964 that a clearer picture of the aqueous vanadium(5) species emerged, resulting from work by both Connor(14) and Howarth(15). The results of their studies are summarized by the following equilibria.

pH < 2 $H_2V_{10}O_{28}^{4-} + 14H^+ \rightleftharpoons 10VO_2^+ + 8H_2O$ [14]

8 > pH > 3 $30(VO_3)^{1-} + 12H^+ \rightleftharpoons 3V_{10}O_{28}^{6-} + 6H_2O$ [15]

$V_{10}O_{28}^{6-} + H^+ \rightleftharpoons HV_{10}O_{28}^{5-} \overset{H^+}{\rightleftharpoons} H_2V_{10}O_{28}^{4-}$ [16]

pH > 8.4 $3V_2O_7^{4-} + 6H^+ \rightleftharpoons 3(VO_3)^{1-} + 3H_2O$ [17]

pH > 13 $2VO_4^{3-} + 2H^+ \rightleftharpoons 2HVO_4^{2-} \rightleftharpoons V_2O_7^{=} + H_2O$ [18]

It is evident from this data that the equilibria are extremely complex, and that the vanadium(5) species is only cationic over a very limited pH range. The main points arising from this work are that vanadium(5) is only completely cationic in very acidic solution (pH < 0.8) and at all other pH's the vanadium(5) species is either anionic or a mixture of cationic and anionic forms. These equilibria indicate only the major vanadium(5) species present at any pH. Thus, at any pH value the vanadium(5) exists as a complex mixture of the above species.

I.C.2. Vanadium(4) Species

The aqueous vanadium(4) species are not as complex as those observed for vanadium(5), but, nevertheless, considerable work has been done in this field(16-20). There is evidence for only one vanadium(4) species, VO^{2+}, in acidic solution(21,22). In basic solution vanadium(4) precipitates as a yellow-brown nonamphoteric hydroxide $VO(OH)_2$ (23). The vanadium(4) can be chelated easily, either with EDTA, tartrate or citrate, giving the following complexes: $VO(TART)^{2-}$ or $VO(TARTH)^{-}$ (24). Once the vanadium(4) has been complexed with a suitable reagent it is then soluble in alkaline solution.

In the Stretford solution either tartrate or citrate is added to complex the vanadium(4) formed during the process.

I.D. Alkyl Phosphene Oxides as Organic Extractants

The development of alkyl phosphine oxides as solvent extractants came as a direct consequence of the need in the U.S.A. for uranium. The United States Atomic Energy Commission needed an efficient method of removing uranium from its ores, as well as a method of recovering uranium from spent nuclear reactor fuel rods. One of the first methods proposed was by solvent extraction using tributyl phosphate dissolved in carbon tetrachloride. Using this as the extractant it was found that in acidic conditions (pH = 2) 54% of the uranium present in the aqueous phase was extracted(25). This result caused researchers in the field to look for more, and perhaps better, organic extractants. The researchers confined themselves initially to organo phosphorous compounds and later to organic amines.

The development of tributyl phosphate as an extractant led to the use of tributyl phosphine oxide as an extractant. It was found that where tributyl phosphate was able to extract 54% of uranium present the tributyl phosphine oxide was capable of extracting 99.7% of the uranium. The very high uranium extraction coefficient caused workers to determine what other elements were extracted by solutions of tributyl phosphine oxide. The final list of elements extracted included uranium, copper, silver, gold, vanadium, zinc and gallium(26). Alkyl phosphine oxides also extracted citrate, tartrate and acetate.

In 1955 Blake(27) found the most effective phosphine oxide for uranium extraction to be trioctyl phosphine oxide, and this is the alkyl phosphine oxide which most research has centered on.

It is found with only one exception (As) that trioctyl phosphine oxide solutions extract elements only in their highest oxidation state. For example, in acid solution vanadium(5) is quantitatively extracted, while under the same conditions vanadium(4) is not extracted at all.

Once the phosphine oxide solution has extracted an element it may be stripped quantitatively by shaking the phosphine oxide solution with 0.5 M sodium carbonate solution. It is believed that the stripping mechanism is simply an exchange or replacement of the extracted species by carbonate.

Experiments have been performed to determine the structure of the extracted species(27) in acid solution, and in all cases the extracted species are of the type $M^{n+}A_n \cdot 2R_3P{=}O$, where M^{n+} is a metal, and A^- is some anion. The combining ratio of phosphine oxide to metal has always been found to be 2:1.

No investigations have been undertaken to determine the extraction coefficients of any extracted species in alkaline solution. However, since the vanadium(5) species present in solution at pH 2.5 is similar to that found at pH 8 (Fig. 8), we may obtain some information as to the extraction coefficient of vanadium(5) in alkaline solution by looking at those found at pH 2.5.

Consider the extraction coefficients of vanadium(5) as a function of pH.

pH	E_a^o	(nitrate = 0.1 M)
1.5	10	
2.0	10	
2.5	1.1	

From this table we see a dramatic decrease in extraction coefficient over the pH range 2.0 → 2.5. This decrease in extraction coefficient coincides with the formation of an anionic vanadium(5) species. It is not unlikely then that since the vanadium(5) species at pH 2.5 is so similar to that at pH 8 we could expect an extraction coefficient at pH 8 of similar magnitude.

Similarly, if we look at the effect of nitrate on the vanadium(5) extraction coefficient at pH 2.5 we should be able to compare this with the effect of nitrate at pH 8.

E_A^o	(NO_3^-)M	pH = 2.5
1.1	0.2	
1.1	0.3	
0.9	0.4	
1.1	0.5	

We see that nitrate has no effect on the vanadium(5) extraction coefficient at pH 2.5.

It appears then that extraction of vanadium(5) from alkaline solution may parallel the extraction characteristics found at pH 2.5 → 3.0.

II. DEVELOPMENT OF THE ANALYTICAL METHOD

II.A. Experimental Details

The primary aim of the work was to develop an analytical procedure for the determination of vanadium(5) in the presence of vanadium(4) in alkaline solution and then to apply the method to the analysis of the Stretford liquor.

As mentioned in Section I.D., Blake found that in acidic media vanadium(5) is quantitatively separated from vanadium(4) by solvent extraction using simple symmetrical aliphatic phosphine oxides dissolved in kerosene. Since the plant operating pH in the Stretford process is 8.5 - 9.5 it was thus decided to extend Blake's study by investigating the extraction characteristics of the vanadium(5) species under alkaline conditions.

The work was undertaken in three stages: firstly, to compare several symmetrical aliphatic phosphine oxides of various hydrocarbon chain lengths in their ability to extract vanadium(5) over the pH range 0 - 12; secondly, to choose conditions such that the extraction of vanadium(5) at pH 9 is maximized; and, thirdly, to apply the analytical procedure to the analysis of the Stretford liquor.

II.A.1. Apparatus

The extraction procedure was performed by using 250-ml pyrex separatory funnels, fitted with teflon stopcocks, and shaken by means of a Burrell wrist action shaker (Burrell Corp., Pittsburgh, Pa.). All spectrophotometric measurements were carried out using a Bausch and Lomb spectronic 600 spectrophotometer, equipped with a Sargent recorder (model S.R.L.).

All volumetric laboratory glassware was of "B" class and used uncalibrated.

II.A.2. Reagents and Solutions

Phosphine oxides were prepared in the laboratory by the method of Kosolapoff(28) (Appendix 1). These were dissolved in kerosene (Fisher Analytical) to the desired concentration.

Buffer solutions were prepared by dissolving sodium carbonate (anhydrous Shawinigan Reagent) and sodium bicarbonate (Baker and Adamson Reagent) in water (Appendix 2).

Vanadium(5) solutions were prepared by dissolving 1 g/l of sodium metavanadate (B.D.H. Reagent) in the appropriate buffer solution.

Vanadium(4) solutions were prepared by dissolving 1 g/l of vanadyl sulfate (Fisher Purified) in buffer containing 12 g/l of sodium citrate (Shawinigan Reagent).

For studies on the effect of nitrate and sulfate concentration on the extraction process appropriate amounts of ammonium nitrate (B.D.H. Analytical) and sodium sulfate (Shawinigan Reagent) were dissolved in buffer solution. A silver amalgam was prepared by dissolving silver that had been previously obtained by precipitation from acidic silver nitrate solution (Baker Analyzed Reagent) by copper foil (B.D.H. Analar). A 0.5 M carbonate solution was prepared by dissolving 53.0 g/l of sodium carbonate (Shawinigan Reagent) in water.

II.A.3. Procedures

II.A.3.a. Comparison of Several Phosphine Oxides in their Ability to Extract Vanadium(5) over the 0-12 pH Range

10.0-ml aliquots of a standard vanadium(5) solution were made 0.3 M in nitrate, and 0.5 M in sulfate by dissolving in them suitable amounts of NH_4NO_3 and Na_2SO_4 respectively. To the resulting solutions 20 ml aliquots of the appropriate phosphine oxide solution were added and the resulting mixtures were shaken for one hour by means of a wrist action shaker (Appendix 3). The two phases were allowed to separate and the aqueous layer drawn off. This was then acidified with 20 ml of a 1:1 hydrochloric nitric acid mixture and evaporated to dryness on a hot plate. The residue was dissolved in 20 ml of 1 M hydrochloric acid, approximately 5 g of silver amalgam added and the mixture was allowed to stand until the blue vanadium(4) colour developed complexely. The mixture was filtered through a Whatmans No. 1 filter paper and the optical density of the filtrate was read at a wavelength of 690 nm using 1 M $HC\ell$ in the reference beam and a path length of 5.0 cm (Appendix 4).

Stripping of the pregnant organic phase was achieved by shaking it for one hour with 20 ml of 0.5 M sodium carbonate solution, and then allowing the mixture to stand overnight at room temperature. The aqueous layer was drawn off, acidified, evaporated to dryness and the colour developed with the silver amalgam as before. The optical density of the blue solution was then read.

II.A.3.b. Studies on the Effect of Phosphine Oxide Concentration on the Percentage of Vanadium(5) Extracted

10.0-ml aliquots of a vanadium(5) solution, at pH 9.16, containing 0.3 M nitrate and 0.5 M sulfate as ammonium nitrate and sodium sulfate were extracted with 20 ml aliquots of trioctyl phosphine oxide ranging in concentration from 0.0 M to 0.7 M.

Analyses for vanadium in both the aqueous and organic phases were performed as usual (see Section II.A.3.a.).

II.A.3.c. Studies on the Effect of Sulfate Concentration on the Percentage of Vanadium(5) Extracted

10.0-ml aliquots of a standard vanadium(5) solution, at pH 9.16 and containing 0.3 M nitrate as ammonium nitrate, were pipetted into 250 ml separatory funnels. To these solutions enough solid sodium sulfate was added such that the final concentration of sulfate ranged from 0.0 M to 0.5 M. These solutions were then extracted with 20 ml aliquots of 0.5 M trioctyl phosphine oxide and then the analyses for vanadium in both phases performed as usual (see Section II.A.3.a.).

II.A.3.d. Studies on the Effect of Nitrate Concentration on the Percentage of Vanadium(5) Extracted

10.0-ml aliquots of standard vanadium(5) solution, at pH 9.16, containing 0.5 M sulfate as sodium sulfate were pipetted into 250 ml separatory funnels. To these solutions enough solid ammonium nitrate was added such that the final concentration of nitrate ranged from 0.0 M to 0.5 M. These solutions were then extracted with 20 ml aliquots of 0.5 M trioctyl phosphine oxide and then the analyses for vanadium in both phases performed as usual (see Section II.A.3.a.).

II.A.3.e. Studies on the Effect of Vanadium(4) on the Extraction of Vanadium(5)

Ten solutions were prepared with the compositions shown in Table 1. In each case the final volume was 10.0 ml and the pH was 9.16. These solutions were each extracted with 20 ml of 0.5 M trioctyl phosphine oxide and then the analyses for vanadium in both phases performed as usual (see Section II.3.A.a.).

Table 1

Composition of Solutions used for Vanadium(5)/(4) Mixtures

% V as V_5	% V as V_4	M of NO_3^-	M of $SO_4^=$	M Citrate
0	100	0.3	0.5	0.047
20	80	0.3	0.5	0.047
40	60	0.3	0.5	0.047
50	50	0.3	0.5	0.047
60	40	0.3	0.5	0.047
80	20	0.3	0.5	0.047
100	0	0.3	0.5	0.047

II.B. Results and Discussion

II.B.1. The Effect of pH, Trialkyl Phosphine Oxide Chain Length, and Some Selected Anions on the Percentage of Vanadium(5) Extracted

From Figs. 5 through 7, which summarize the data found in the pH studies, we observe a distinct minima through extraction by trihexyl, trioctyl and tridecyl phosphine oxide solutions in the pH range 2-8. To explain this data it is necessary to look firstly at the types of species extracted by phosphine oxides, and secondly at the possible vanadium(5) species present at any given pH.

It was found by Blake and others that the species migrating across the phase boundary between acidic aqueous vanadium(5) solutions and phosphine oxides dissolved in kerosene could be represented as

$VO_2^+Cl^- \cdot 2R_3P = 0$ or, more generally, as

$M^{n+}A_n^- \cdot 2R_3P = 0$

where M^{n+} may be VO_2^+, and A^- is usually Cl^- or NO_3^-. However, the vanadium(5) species present in solution is dependent on pH and ranges between two extremes, namely VO_2^+ in very acidic solution and VO_4^{3-} in highly alkaline solution. Clearly, in alkaline solution, vanadium(5) can no longer be extracted as VO_2^+ and it is necessary, then, to propose a structure of the type $M^{n+}A_n^- \cdot YR_3P = 0$ where M^{n+} is now Na^+ and A^- may be VO_3^- or VO_4^{3-}.

From Table 2 we can identify the vanadium(5) species present at any pH. Fig. 8 shows a plot of the charge/ionic weight of vanadium(5) species ratio vs pH. The general shape of this graph is similar to that obtained by plotting percentage of vanadium(5) extracted vs pH (Figs. 5-7). Thus, we propose that the phosphine oxides tend to extract vanadium species that have a high charge/

Fig. 5. Percentage Of Vanadium (5) Extracted Vs pH For Extraction With 0.5M Trihexyl Phosphine Oxide Solution.

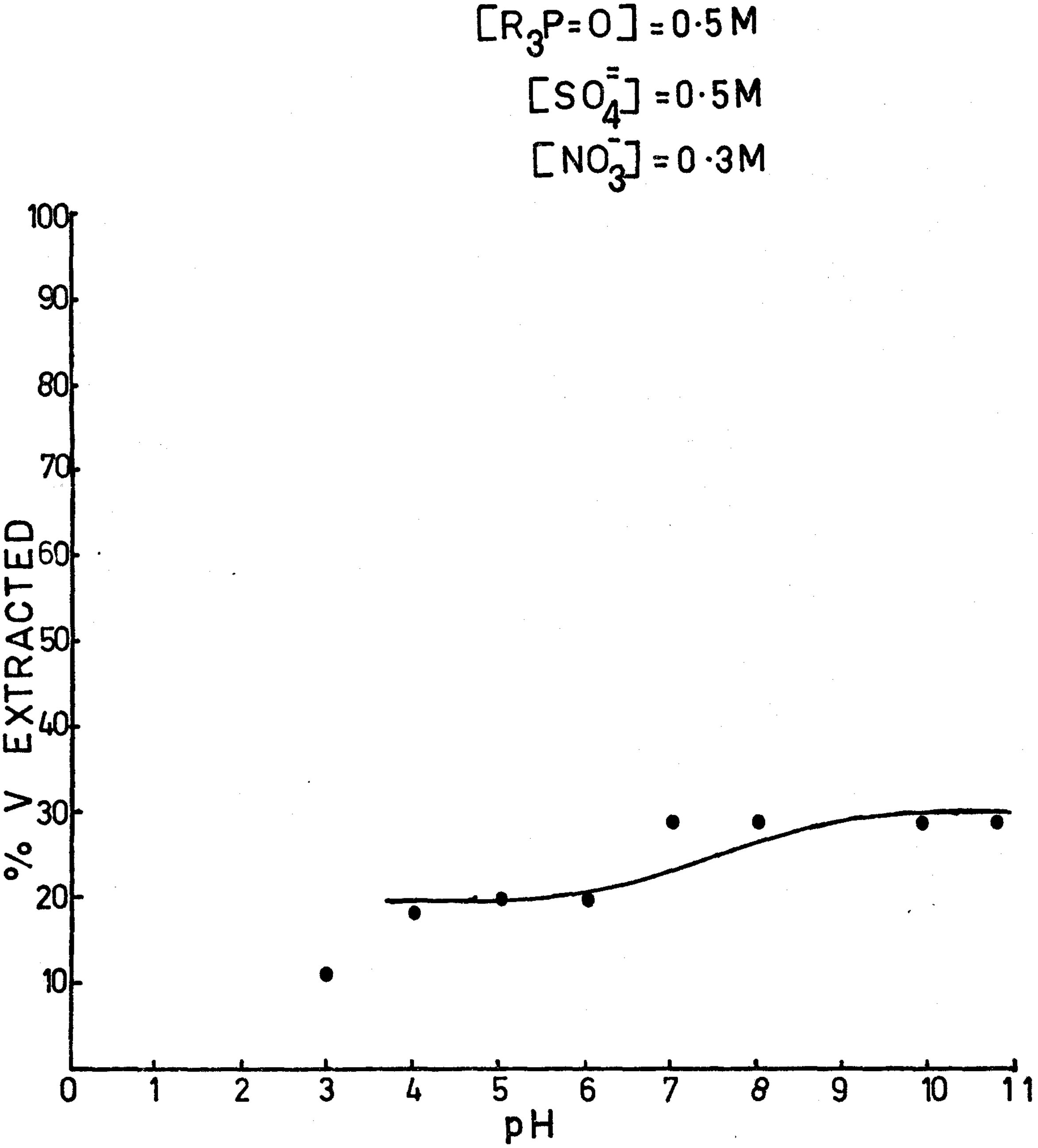

[R3P=O] = 0·5 M
[SO4=] = 0·5 M
[NO3-] = 0·3 M
% V EXTRACTED
100
90
80
70
60
50
40
30
20
10
0
1
2
3
4
5
6
7
8
9
10
11
pH

Fig. 6. Percentage Of Vanadium (5) Extracted Vs pH For Extraction With 0.5M Trioctyl Phosphine Oxide Solution.

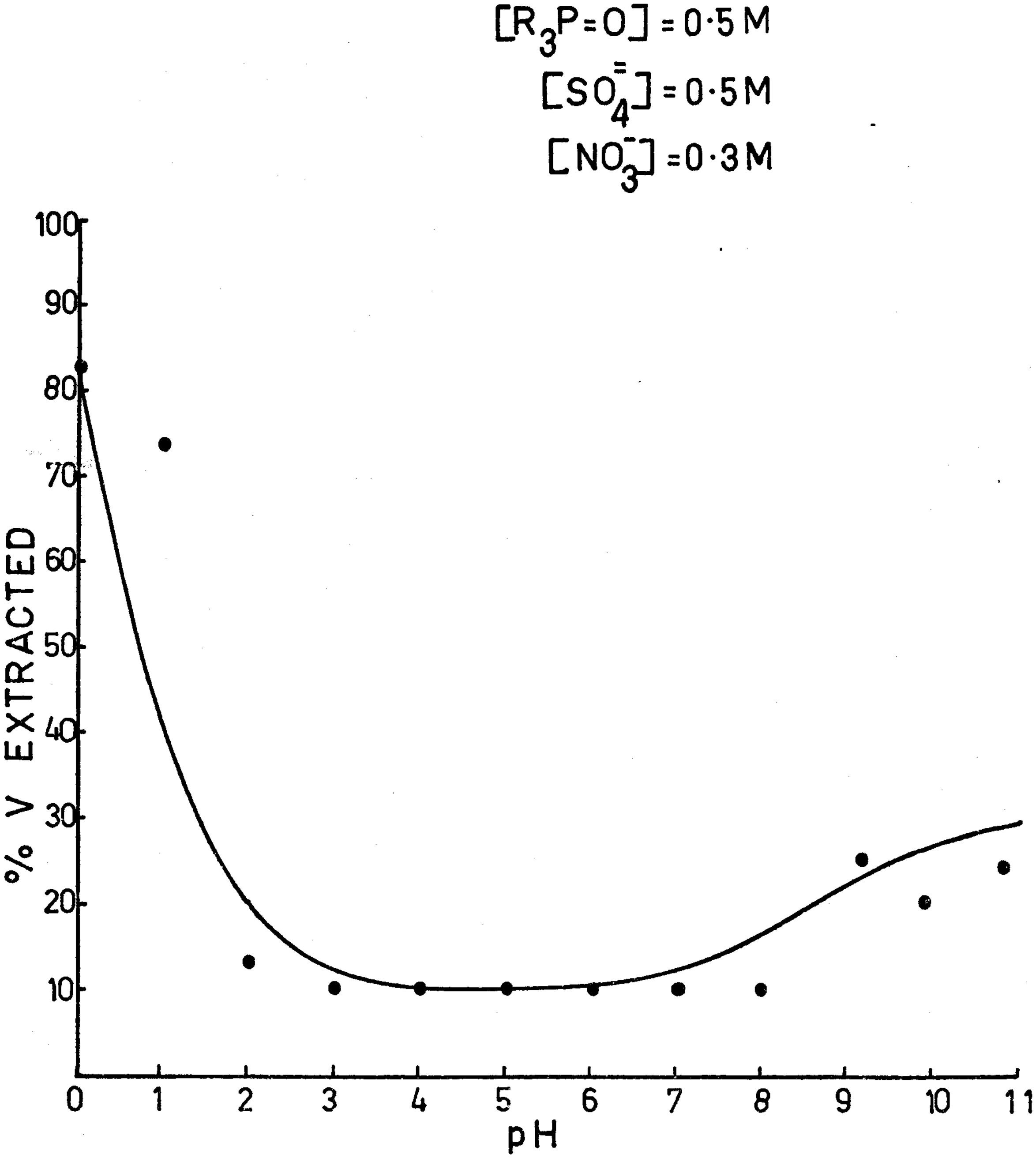

$[R_3P=O] = 0{\cdot}5\,M$
$[SO_4^{=}] = 0{\cdot}5\,M$
$[NO_3^{-}] = 0{\cdot}3\,M$
% V EXTRACTED
100
90
80
70
60
50
40
30
20
10
0
1
2
3
4
5
6
7
8
9
10
11
pH

Fig. 7. Percentage Of Vanadium (5) Extracted Vs pH For Extraction With 0.5M Tridecyl Phosphine Oxide Solution.

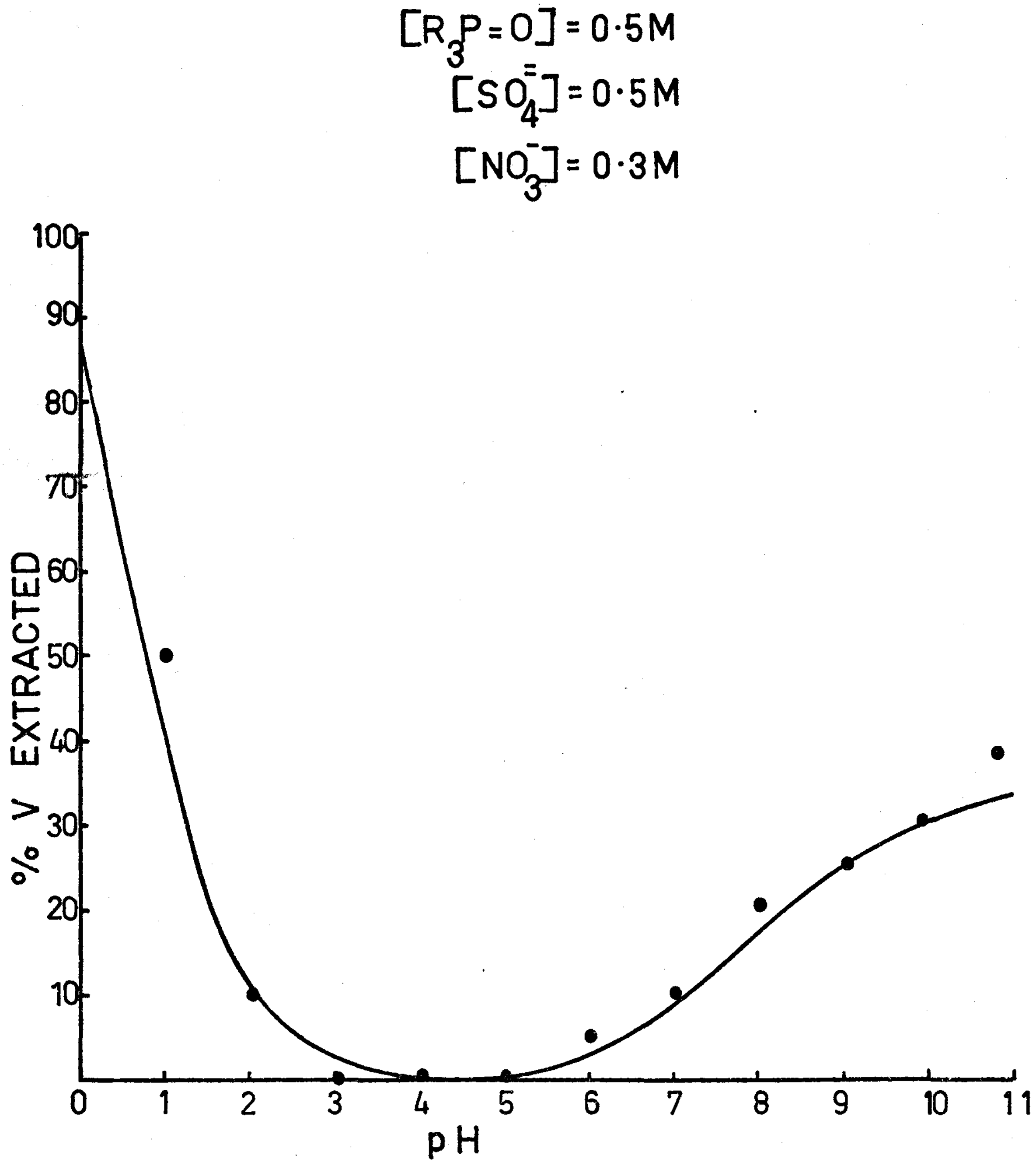
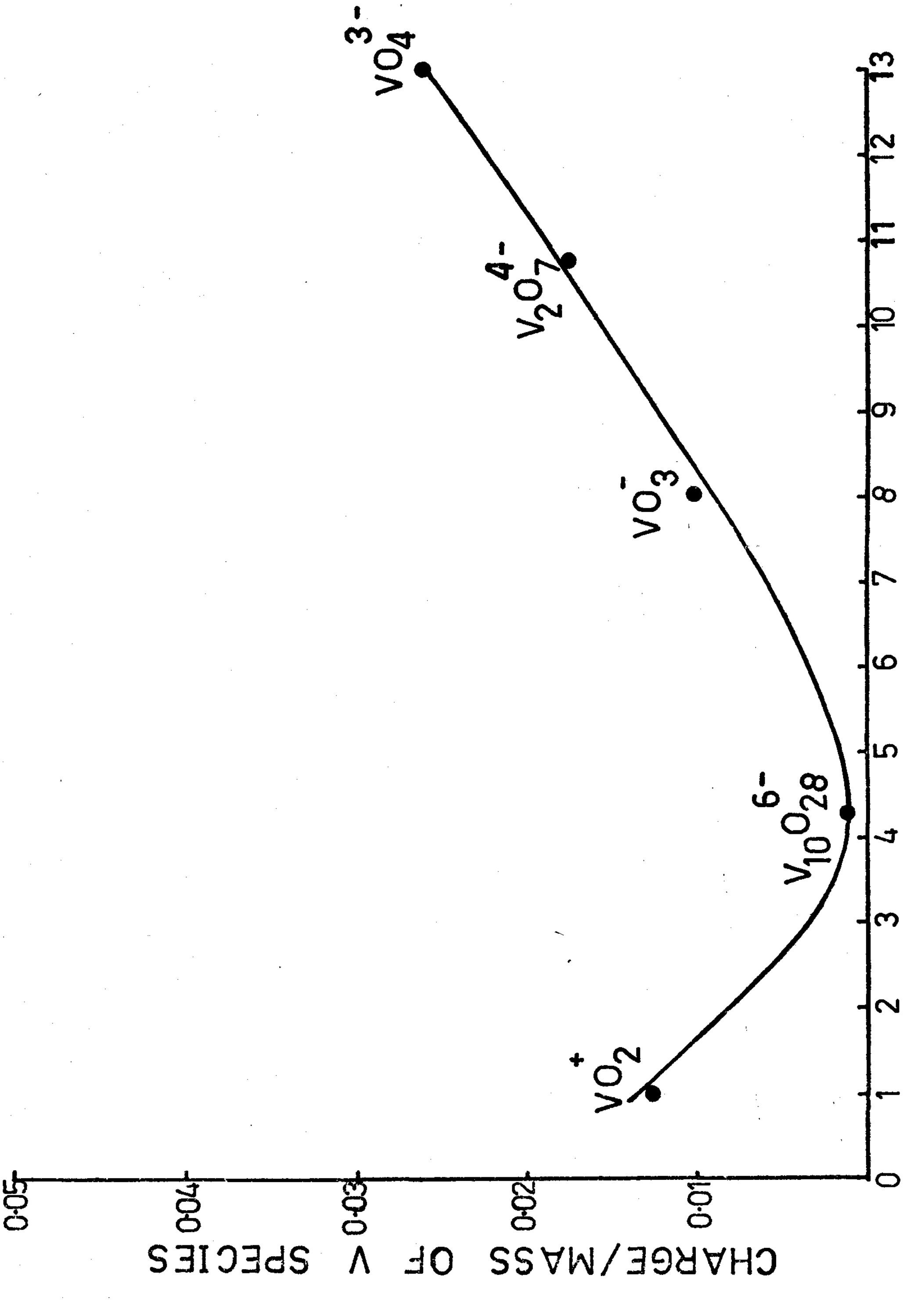

[R₃P=O] = 0·5M
[SO₄⁼] = 0·5M
[NO₃⁻] = 0·3M
% V EXTRACTED
100
90
80
70
60
50
40
30
20
10
0
1
2
3
4
5
6
7
8
9
10
11
pH

Table 2

Vanadium(5) Species Present in Aqueous Solution in Various pH Ranges

pH	Species		Colour
>12.6	orthovanadate	VO_4^{3-}	colourless
9.6-12.6	pyrovanadate	$V_2O_7^{4-}$	colourless
6.5- 9.6	metavanadate	VO_3^-	colourless
2.0- 6.5	polyvanadate	$V_{10}O_{23}^{6-}$	orange
< 2	dioxyvanadium	VO_2^+	yellow

Fig. 8. Plot Of Charge/ Ionic Mass Of Vanadium (5) Species Present In Aqueous Solution Vs pH.



CHARGE/MASS OF V SPECIES
0·05
0·04
0·03
0·02
0·01
0
1
2
3
4
5
6
7
8
9
10
11
12
13
pH
VO_2^+
$V_{10}O_{28}^{6-}$
VO_3^-
$V_2O_7^{4-}$
VO_4^{3-}

ionic mass ratio. Furthermore, the extraction is largely independent of sign.

Generally at any given pH solutions of the lower molecular weight phosphine oxides tend to extract vanadium(5) to a much greater extent than those of higher molecular weight. However, the solubility of the lower molecular weight phosphine oxides in water is greater at all pH values. Thus, in selecting a phosphine oxide for use as an analytical reagent it is necessary to weigh the solubility of the phosphine oxide in water against its ability to extract. Since for an industrial solvent extraction process the extractant undergoes a cyclic process, i.e., extraction → stripping → extraction, it is necessary to minimise the losses of extractant. With this in mind, trioctyl phosphine oxide was chosen as that phosphine oxide which possessed the most useful qualities. Consequently all further studies undertaken dealt solely with kerosene solutions of it as the extractant.

From the initial study on the effect of pH upon the percentage of vanadium(5) extracted it was proposed that the vanadium(5) species extracted was anionic, i.e., VO_3^-. It follows then that the addition of some other anions may decrease the percentage of vanadium(5) extracted. The anions chosen in this study have been previously shown(27) to effect the vanadium(5) extraction coefficient in acidic media. The results for the affect of nitrate and sulfate on percentage of vanadium(5) extracted are shown in Figs. 9 and 10. From these graphs it can be seen that the extraction is unaffected by the addition of either of these anions. However, the addition of citrate causes a marked decrease in the extraction of vanadium(5) as shown in Table 3. It has been shown by other workers(25) that citrate is extracted by phosphine oxides. Similarly when the carbonate concentration is increased from 0.01 M to 0.5 M the amount of vanadium(5) extracted drops to zero. This latter

Fig. 9. Effect Of Sulfate On Percentage Of Vanadium (5) Extracted By Trioctyl Phosphine Oxide Solution.

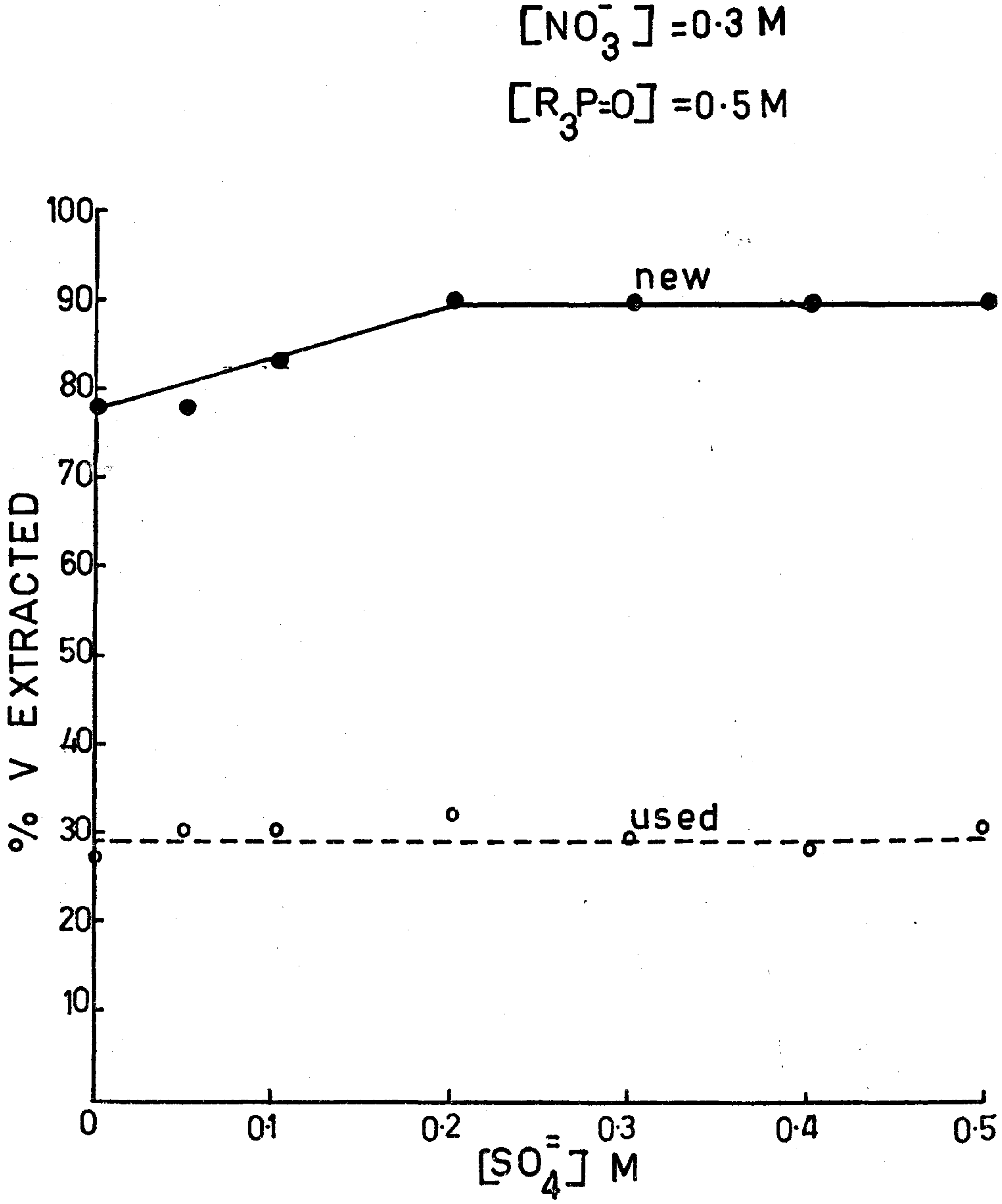

[NO3-] =0·3 M
[R3P=O] =0·5 M
% V EXTRACTED
100
90
80
70
60
50
40
30
20
10
0
0·1
0·2
0·3
0·4
0·5
[SO4=] M
new
used

Fig. 10. Effect Of Nitrate On Percentage Of Vanadium (5) Extracted By Trioctyl Phosphine Oxide Solution.

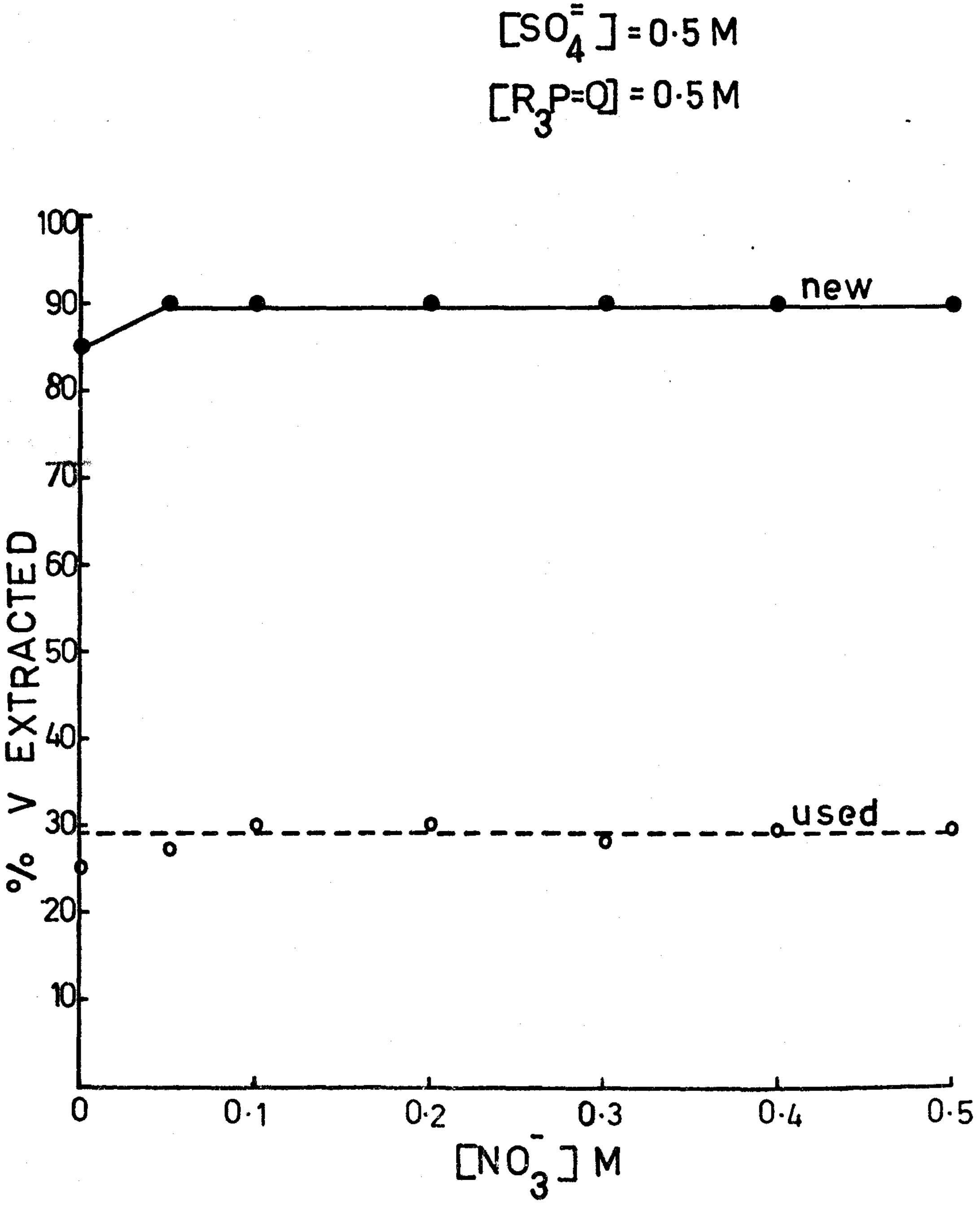

[SO$_4^=$] = 0·5 M
[R$_3$P=O] = 0·5 M
% V EXTRACTED
100
90
80
70
60
50
40
30
20
10
0
0·1
0·2
0·3
0·4
0·5
new
used
[NO$_3^-$] M

Table 3

Effect of Citrate and Carbonate on % of Vanadium(5) Extracted

Citrate conc. M	Carbonate conc. M	Percentage Vanadium(5) Extracted
0.0 M	0.01	87.0 ± 5 (abs)
0.0 M	0.5	0.0
0.047M	0.01	30.8 ± 5 (abs)

observation leads to an explanation of why the fresh phosphine oxide solutions are much better extractants than those that have been used. If we consider that the stripping procedure to be a replacement process, where the vanadium in the organic phase is replaced by carbonate from the aqueous stripping phase. Then once the phosphine oxide solution has been in contact with 0.5 M sodium carbonate it becomes "saturated" with carbonate, and thus unable to extract any vanadium(5). This effect would not be noticed when working in acidic conditions, as the phosphine oxide would become "regenerated" during the next extraction process.

By analysis of the results we have obtained from our study on the effect of pH on the vanadium(5) extraction, it is possible to obtain a picture of the extracted species. It is likely then that the extracted species in alkaline solution is $Na^{+}(VO_3^{-}) \cdot YR_3P{=}0$ or $Na_{3x}(VO_4^{3-})_x \cdot YR_3P{=}0$ or more likely a mixture of both.

II.B.2. The Effect of Phosphine Oxide Concentration on Percentage of Vanadium(5) Extracted

From Fig. 11 we can see that the extraction of vanadium(5) is dependent on the concentration of phosphine oxide over the range 0.0 to 0.5 M. Once a concentration of 0.5 M is reached no further change in extraction coefficient is found, regardless of phosphine oxide concentration. This value of 0.5 M trioctyl phosphine oxide has also been observed by Blake to optimize vanadium(5) extraction.

The results obtained from this study also yield an insight into the extracted species(11,12). Consider our system which may be represented by

$$M^{L-}_{aq} + LA^{+}_{aq} + N(S)_{org} \rightleftharpoons [MA_L \cdot NS]_{org}$$

where M^{L-}_{aq} is in our case VO_3^-;

A^+_{aq} is in our case Na^+; and

S_{org} is in our case the phosphine oxide.

Then the overall equilibrium constant is given by

$$K_M = \frac{[MA_L \cdot NS]_{org}}{[M^{L-}]_{aq}[A^+]_{aq}[S]^N_{org}} \quad .$$

which yields

$$K'_M = \frac{E}{[S]^N_{org}} \quad .$$

Taking logs

$$N \log[S]_{org} = \log E + \text{const.}$$

Then a plot of log[S] vs logE should give a straight line with slope N. For [S] we use the concentration of phosphine oxide solution. This plot is shown in Fig. 12 and has a slope equal to 2.3. This indicates that our extracted species is of the type

$$NaVO_3 \cdot 2R_3P = O$$

which is analogous to that found by Blake in his study of the combining ratio of phosphine oxide to uranium in acidic solution.

II.B.3. The Effect of Vanadium(4) Concentration on Percentage of Vanadium(5) Extracted

To determine the effect of the vanadium(4) concentration on the vanadium(5) extraction coefficient a series of vanadium(5)/(4) standard solutions were prepared. These solutions were then extracted with trioctyl phosphine oxide solution. In this experiment it is possible to calculate the expected optical density at stages (1) and (2) in Fig. 13. This was done as follows. Before extraction

optical density of 10 ml of standard V(5) = 0.390

optical density of 10 ml of standard V(4) = 0.465.

% V(5)	% V(4)	Optical density of aqueous phase (1) after extraction
100	0	0.270
80	20	0.300
60	40	0.315
50	50	0.350
40	60	0.375
20	80	0.410
0	100	0.480

Now the percentage of V(5) extracted from solution containing 100% V(5)

$$= \frac{(0.390 - 0.270)}{0.390} \times 100\%$$

= 30.7% extracted.

For the purpose of our calculation we assume that in every solution 30.7% of the vanadium(5) is extracted and 0% of vanadium(4) is extracted. We can then calculate what the expected optical densities of the solutions after extraction should be.

Consider the solution containing 50% vanadium(5) and 50% vanadium(4). The total optical density before extraction should be the sum of the optical densities of the parts.

$$\text{optical density due to vanadium(5)} = \frac{0.390}{10} \times 5 = 0.195$$

$$\text{optical density due to vanadium(4)} = \frac{0.465}{10} \times 5 = 0.232$$

Therefore before extraction the optical density of the solution should be 0.427. Now if 30.7% of the vanadium(5) is extracted the optical density of the solution remaining after extraction should be

$$\frac{0.390}{10} \times \frac{5}{1} \times \frac{0.693}{1} + \frac{0.465}{10} \times 5 = 0.367.$$

From the experimental results we see the actual optical density found was 0.350.

Similarly for the stripped solution we know that the expected optical density is $\frac{0.39}{10} \times \frac{5}{1} \times 0.307 = 0.06$, and the experimentally determined value is 0.09.

By performing the appropriate calculation on the other solutions we can determine the expected optical densities, in both the extracted and stripped solutions. The results of the calculations are shown as a graph in Fig. 14.

Since good agreement was obtained for the experimental and calculated values it is possible to draw four conclusions from the data.

(a) No vanadium(4) is extracted by trioctyl phosphine oxide solutions at pH 9.16.

(b) The percentage of vanadium(5) extracted is independent of vanadium(5) concentration over the range studied.

(c) The percentage of vanadium(5) extracted is independent of the vanadium(4) concentration over the range studied.

(d) Large excesses of phosphine oxide have no effect on the extraction of vanadium(5).

Fig. 11. Effect Of Trioctyl Phosphine Oxide Concentration On Percentage Of Vanadium (5) Extracted.

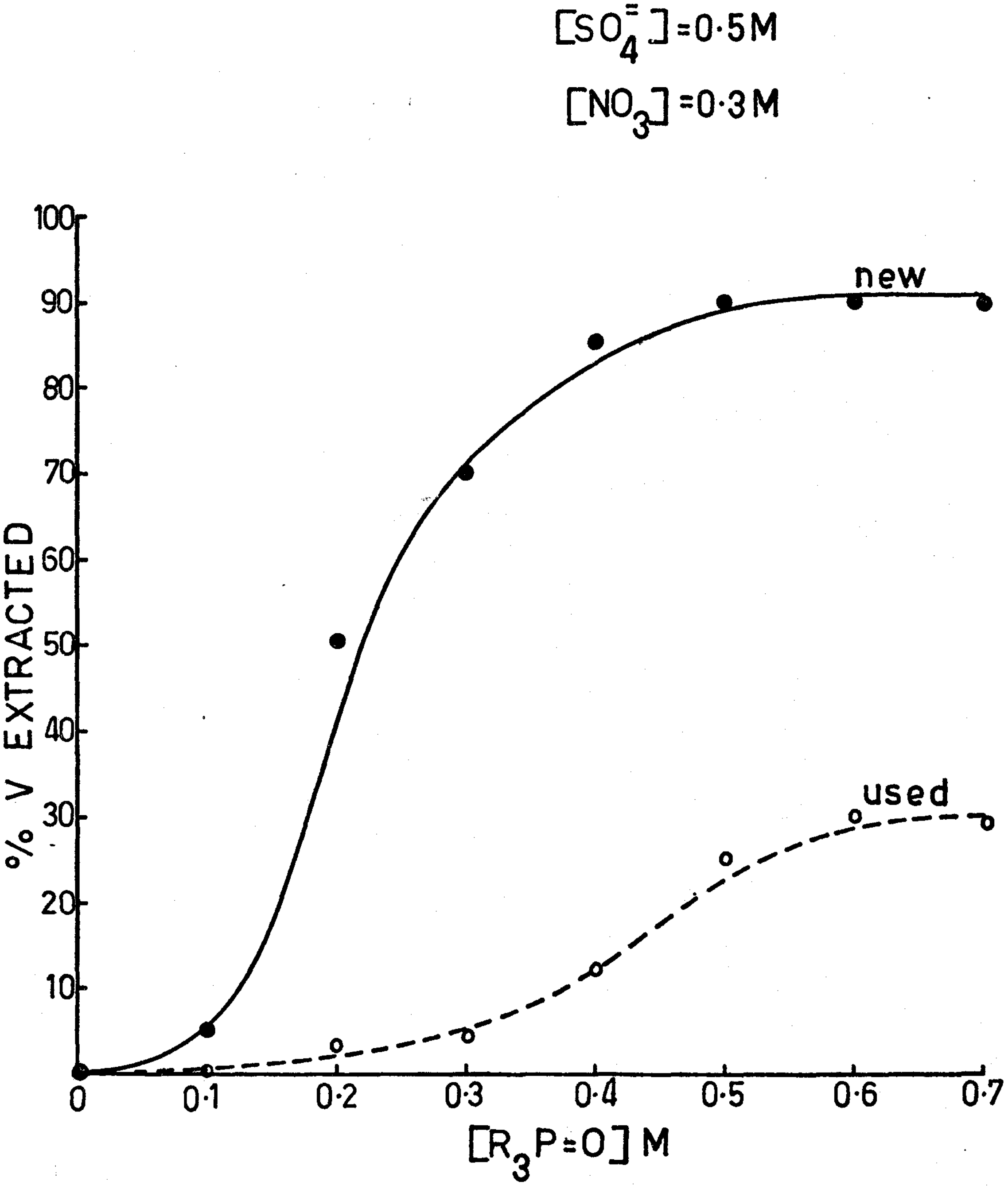

$[SO_4^=] = 0\cdot5M$
$[NO_3] = 0\cdot3M$
new
used
% V EXTRACTED
100
90
80
70
60
50
40
30
20
10
0
0·1
0·2
0·3
0·4
0·5
0·6
0·7
$[R_3P=O]$ M

Fig. 12. Plot Of Log Extraction Coefficient Vs Log Trioctyl Phosphine Oxide Concentration.

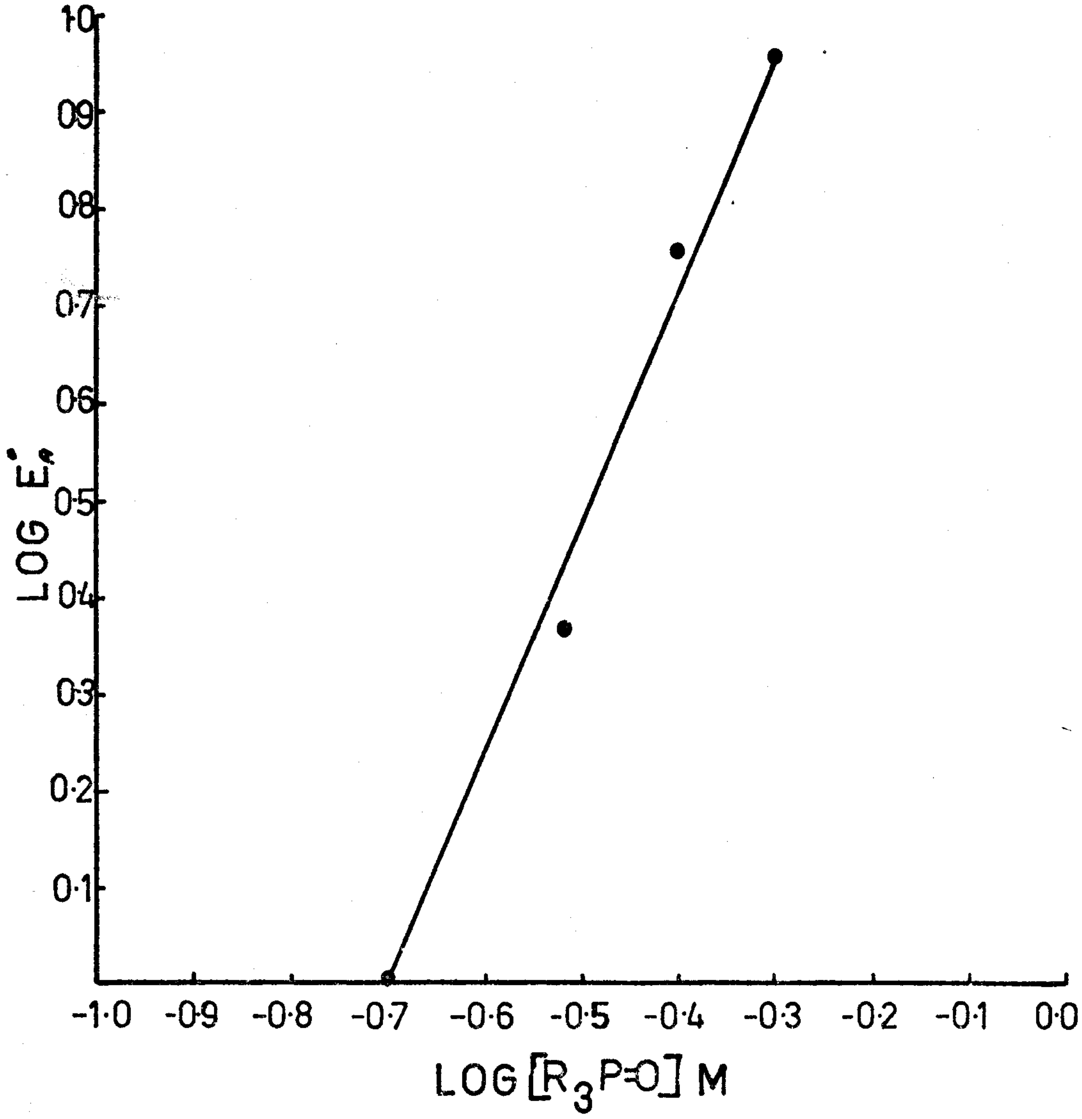

1·0
0·9
0·8
0·7
0·6
0·5
0·4
0·3
0·2
0·1
LOG E'
-1·0
-0·9
-0·8
-0·7
-0·6
-0·5
-0·4
-0·3
-0·2
-0·1
0·0
LOG [R3P=O] M

Fig. 13. Flow Chart Of Experimental Procedures.

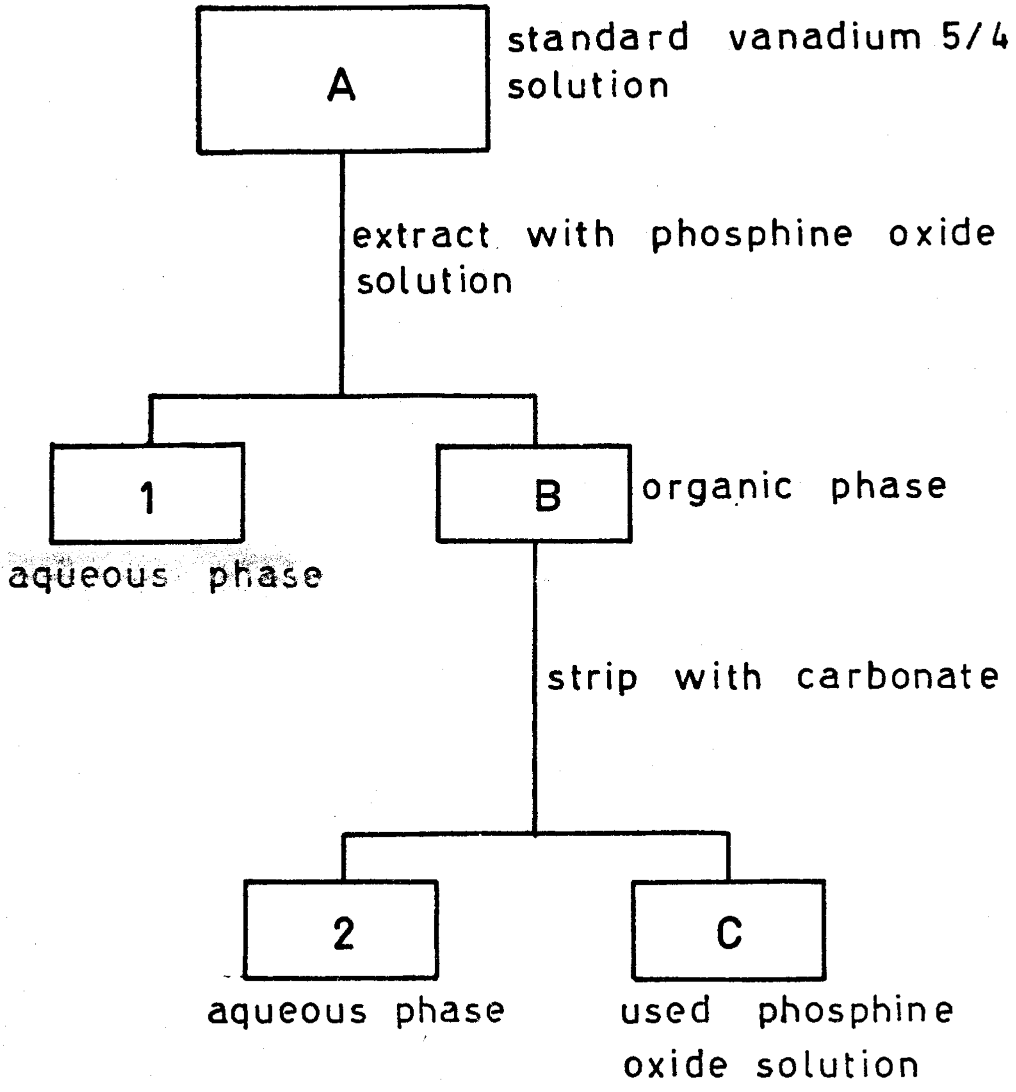
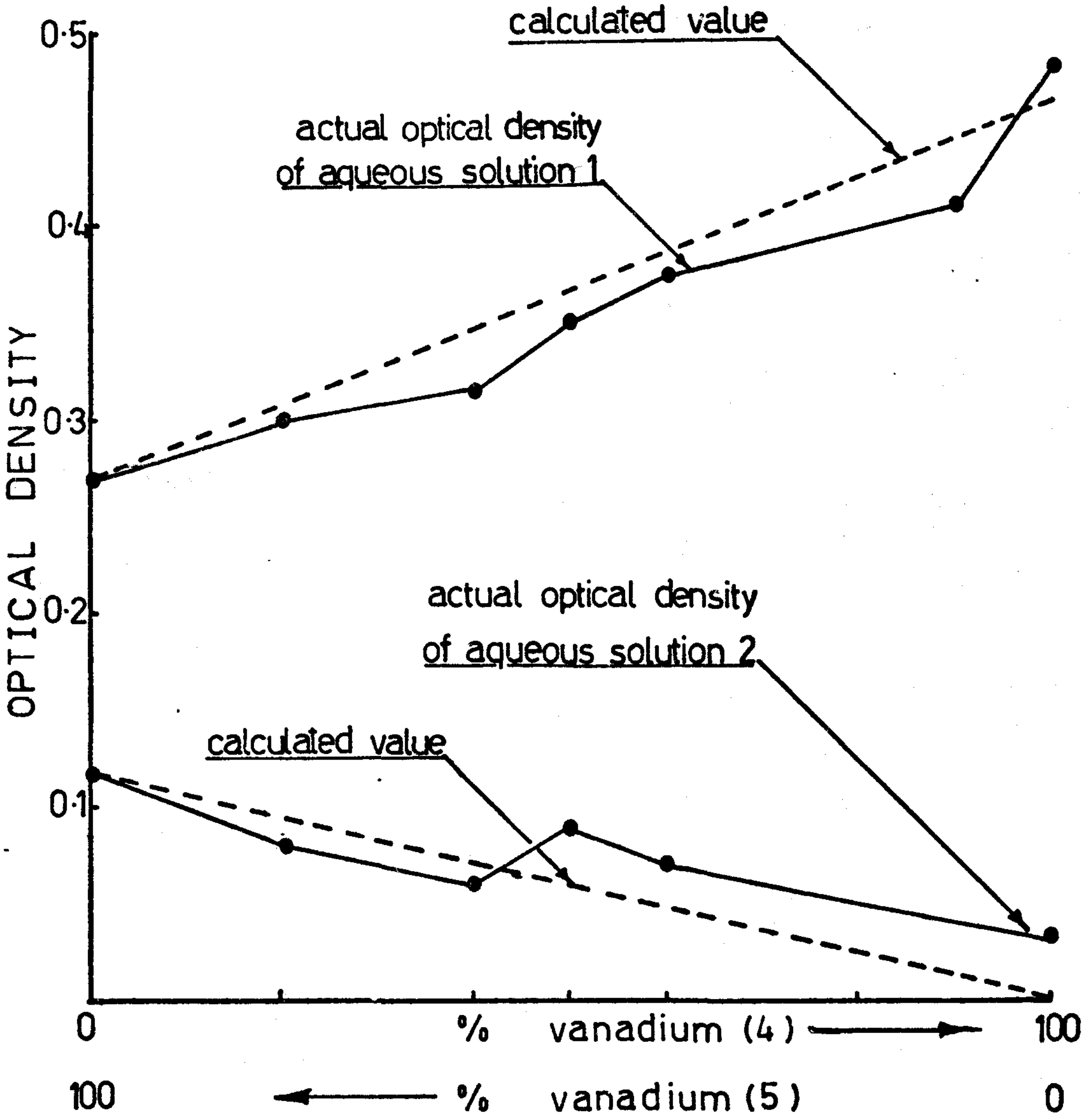

A
standard vanadium 5/4 solution
extract with phosphine oxide solution
1
aqueous phase
B
organic phase
strip with carbonate
2
aqueous phase
C
used phosphine oxide solution

Fig. 14. Plot Of Experimental And Calculated Optical Densities Of Vanadium (5)/(4) Mixtures.


calculated value
actual optical density of aqueous solution 1
actual optical density of aqueous solution 2
calculated value
OPTICAL DENSITY
0·5
0·4
0·3
0·2
0·1
0
% vanadium (4) →
100
100
← % vanadium (5)
0

These four conclusions indicate conclusively that solvent extraction should be an effective analytical means of determining vanadium(5) in the presence of vanadium(4) under alkaline conditions.

II.C. Summary

The analytical procedure developed in Section II.A.3.a. for analysis of a synthetic Stretford liquor was found to be an effective method of estimating vanadium(5) in the presence of vanadium(4). The extraction coefficients found for fresh trioctyl phosphine oxide solutions were high and reproducible. A sample of the experimental results obtained for the extraction of solutions containing only vanadium(5) and 0.3 M in nitrate and 0.5 M in sulfate by 0.5 M trioctyl phosphine oxide are shown in Table 4. An analysis of all the experimental data from a series of thirty such extractions yields the following:

percentage vanadium(5) extracted = 87.0 ± 5.5% (abs.),
percentage vanadium(5) remaining = 15.0 ± 5.0% (abs.), and
mass balance = 102 ± 7.4% (abs.).

Analysis of mass balance data obtained under all experimental conditions gives an overall value of 100.8 ± 7.0% (abs.).

Results obtained during the extraction of vanadium(5) by recycled phosphine oxide solution (see Table 5) are comparable to those found by Brown(27) and others in their studies of the stripping of vanadium(5) from the organic phase by dilute carbonate solutions.

Trioctyl phosphine oxide was found to extract carbonate and citrate in alkaline solution, with a subsequent decrease in the vanadium(5) extraction coefficient.

0.5 M trioctyl phosphine oxide solutions did not extract vanadium

Table 4

Sample of Experimental Results Obtained by Extraction of a Solution Containing only V^5, 0.3 M NO_3^-, 0.5 M $SO_4^=$ by Fresh 0.5 M Trioctyl Phosphine Oxide Solution

Percentage of V^5 Remaining after Extraction	Percentage of V^5 Stripped from $R_3P = 0$	Σ
10 ± 5 %(abs.)	92 ± 5.5% (abs.)	102 ± 7% (abs.)
12 ± 5	91 ± 5.5	103 ± 7
20 ± 5	80 ± 5.5	100 ± 7
22 ± 5	84 ± 5.5	106 ± 7
16 ± 5	85 ± 5.5	101 ± 7
16 ± 5	83 ± 5.5	99 ± 7

Table 5

Sample of Experimental Results Obtained by Extraction of a Solution Containing only V^5, 0.3 M NO_3^-, 0.5 M SO_4^5, by Used Trioctyl Phosphine Oxide Solution

Percentage of V^5 Remaining after Extraction	Percentage of V^5 Stripped from $R_3P = 0$	Mass Balance
69.4 ± 5.0%(abs.)	27.0 ± 5.5%(abs.)	96.4 ± 7.0%(abs.)
71.0 ± 5.0	29.1 ± 5.5	100.1 ± 7.0
72.2 ± 5.0	29.7 ± 5.5	101.9 ± 7.0
78.6 ± 5.0	25.4 ± 5.5	104.0 ± 7.0

alkaline from solutions even when the molar ratio of trioctyl phosphine oxide:vanadium(4) was 1000:1.

III. APPLICATION OF THE ANALYTICAL METHOD TO THE STRETFORD LIQUOR

III.A. Experimental Details

The application of the solvent extraction procedure to the analysis of the Stretford liquor was undertaken in three main stages: firstly, extraction of oxidized Stretford liquor by both fresh and used trioctyl phosphine oxide solution; secondly, determination of some salts extracted by trioctyl phosphine oxide solution; and finally extraction of a reduced Stretford liquor.

III.A.1. Apparatus

The apparatus used for studies on the Stretford liquor was the same as that used in studies on the synthetic liquor (see Section II.A.1.).

III.A.2. Reagents and Solutions

A sample of used Stretford liquor was obtained from the Dominion Foundry and Steel Company.

A 30% sodium hydroxide solution was prepared by dissolving 300 g/l of sodium hydroxide (McArthur Chemical Co. Reagent) in water.

For determinations of anthraquinone disulphonic acid 0.1 g of solid sodium dithionite (B.D.H. Reagent) was added to the solution under test.

A 0.5 M sodium carbonate solution was prepared by dissolving 53.0 g/l of sodium carbonate (Shawinigan Reagent) in water.

III.A.3. Procedures

III.A.3.a. Determination of the Percentage of Vanadium(5) Extracted by Both Fresh and Used Trioctyl Phosphine Oxide Solutions

The Stretford liquor was oxidized by bubbling air through the solution for twenty-four hours. The oxidized Stretford liquor was then filtered through a Whatman's No. 1 filter paper and 10.0 ml aliquots of the filtrate were pipetted into separate 250 ml separatory funnels. To each of these solutions a 20.0 ml aliquot of 0.5 M trioctyl phosphine oxide solution was added. The resulting mixture was then shaken by means of a wrist action shaker for 1 hour. The two phases were allowed to separate, and the aqueous layer drawn off. This was then cautiously acidified with 20 ml of 1:1 hydrochloric-nitric acid mixture and evaporated to dryness on a hot plate.

The residue was treated with a small amount of concentrated nitric acid. If any oxides of nitrogen were observed the residue was dissolved in 20 ml of 1:1 nitric-hydrochloric acid mixture and evaporated to dryness. This procedure was continued until no further oxidation of the residue was observed when treated with concentrated nitric acid. At this stage 5 ml of 70% perchloric acid were added to the residue and the solution was again evaporated to dryness. The residue was then dissolved in 20.0 ml of 1M hydrochloric acid and approximately 5 g of silver amalgam added. The blue colour was allowed to develop and the optical density read as before (see Section II.A.3.a.).

Stripping of the organic phase was achieved by shaking with 20 ml of 0.5 M sodium carbonate solution, and allowing the mixture to stand overnight. The aqueous layer was drawn off, acidified and then the blue colour was developed and measured as usual.

III.A.3.b. Determination of the Total Salts Extracted by Trioctyl Phosphine Oxide

Total dissolved salts in the Stretford liquor were found by pipetting 20.0 ml of filtered Stretford liquor into previously weighed beakers. These solutions were slowly evaporated to dryness on a hot plate, and the beakers placed in an oven at 130° overnight. The beakers were allowed to cool, and reweighed. The total dissolved salts in the Stretford liquor was then calculated.

10.0 ml aliquots of filtered, oxidized, Stretford liquor were pipetted into 250 ml separatory funnels. To each of these solutions 20 ml of 0.5 M trioctyl phosphine oxide solution were added. The solutions were shaken for 1 hour by means of a wrist action shaker. The two phases were allowed to separate, and the aqueous layer withdrawn into a previously-weighed beaker. The solution was slowly evaporated to dryness on a hot plate and the beaker placed in an oven at 130° overnight. The beaker was allowed to cool to room temperature and reweighed. The percentage of salts extracted by 0.5 M trioctyl phosphine oxide solution was then calculated by difference.

III.A.3.c. Determination of the Amount of Anthraquinone Disulfonic Acid Extracted by 0.5 M Trioctyl Phosphine Oxide

5.0 ml of filtered, oxidized, plant liquor were pipetted into a 500-ml volumetric flask. To this, 10.0 ml of 30% sodium hydroxide solution were added. The solution was then diluted to volume with deionized water and approximately 0.1 g of solid sodium dithionite added. The optical density of the solution was then read at a wavelength of 400 nm using a sample path length of 1 cm and water as reference.

10.0 ml aliquots of the filtered, oxidized plant liquor were pipetted into 250 ml separatory funnels. To these solutions 20.0 ml of 0.5 M trioctyl phosphine oxide solution added. The resulting mixture was shaken by means of a wrist action shaker for 1 hour. The two phases were allowed to separate and 5.0 ml of the aqueous layer drawn off and pipetted into a 500-ml volumetric flask. 10.0 ml of 30% sodium hydroxide solution were added and the resulting mixture diluted to volume with deionized water. Approximately 0.1 g of sodium dithionite was added and optical density of this solution was read as before.

III.A.3.d. Extraction of a Reduced Stretford Liquor

Hydrogen sulfide gas was bubbled through the Stretford solution until the oxidation potential of the liquor became constant. The reduced liquor was allowed to stand for approximately ten minutes and then filtered. Ten ml aliquots of the filtered-reduced liquor were pipetted into 250 ml separatory funnels. To each of these solutions 20.0 ml of 0.5 M trioctyl phosphine oxide solution were added. The resulting mixture was shaken for 1 hour. The two phases were allowed to separate and the aqueous layer drawn off. Analysis for vanadium in this aqueous phase was performed as usual (see Section III.A.3.a.).

Stripping of the organic phase was achieved by shaking with 20.0 ml of 0.5 M sodium carbonate solution and allowing the mixture to stand overnight. The aqueous layer was drawn off, acidified and then the blue colour was developed and measured as usual (see Section II.A.3.a.).

III.B. Results and Discussion

III.B.1. Percentage of Vanadium(5) and Dissolved Salts Extracted from the Oxidized Stretford Liquor

Tables 6 and 7 list the results obtained by extraction of the Stretford liquor with both fresh unused and recycled trioctyl phosphine oxide solution. It is found that the fresh phosphine oxide solution is a better extractant of vanadium(5) than the recycled solution. These observations confirm those found in Section III.B.1. and are attributed to saturation of the phosphine oxide

Table 6

Extraction of Vanadium(5) by Fresh Trioctyl Phosphine Oxide Solution

Percentage V^5 Remaining after Extraction	Percentage V^5 Found in Phosphine Oxide Phase	Mass Balance
62.5 ± 5.0%(abs.)	39.0 ± 5.5%(abs.)	101.5 ± 7.0%(abs.)
62.5 ± 5.0	42.0 ± 5.5	104.5 ± 7.0
*46.0 ± 5.0	42.0 ± 5.5	
47.5 ± 5.0	58.0 ± 5.5	105.5 ± 7.0

*Sample spilt.

Table 7

Extraction of Vanadium(5) by Used Trioctyl Phosphine Oxide Solution

Percentage V^5 Remaining after Extraction	Percentage V^5 Found in Phosphine Oxide Solution	Mass Balance
75.0 ± 5.0%(abs.)	21.1 ± 5.5%(abs.)	96.1 ± 7.0%(abs.)
83.0 ± 5.0	10.0 ± 5.5	93.0 ± 7.0
91.0 ± 5.0	12.5 ± 5.5	103.5 ± 7.0
87.0 ± 5.0	16.6 ± 5.5	103.6 ± 7.0

solution by carbonate ions during the stripping procedure.

The vanadium(5) extraction coefficient found from the data taken during extraction of the Stretford liquor with fresh trioctyl phosphine oxide solution was lower than those obtained from extraction of the synthetic liquor. We have previously observed that the vanadium(5) extraction coefficient may be affected by the presence of some anions (see Section II.B.1.). It is then probable that the extraction coefficient is decreased due to the presence of some other extractable species in the Stretford liquor. This hypothesis may be tested by considering two observations. Firstly, consider the percentage of dissolved salts extracted from the Stretford liquor by trioctyl phosphine oxide solution. These results are shown in Table 8 and we can see from these that the trioctyl phosphine oxide solution extracts 14.1% of the total dissolved salts from the Stretford liquor. If we subtract from this figure the percentage due to vanadium(5) we arrive at a corrected value of 14.0%; this is then the percentage other salts extracted by trioctyl phosphine oxide. Secondly, when the organic phase is stripped by aqueous carbonate solution and the resulting aqueous phase is then acidified, a red colouration is produced in the solution and later sulfur is precipitated. This observation indicates the presence of SCN^- and $S_2O_3^=$, both of which are present in the original Stretford solution.

If we combine the results obtained in this study with those obtained by others(25,26,27) it is possible to construct a qualitative picture of the species being extracted from the Stretford liquor (see Fig. 15). We see that the extracted species include $CO_3^=$, HCO_3^-, VO_3^-, SCN^-, $S_2O_3^=$, citrate$^=$. Because of the phosphine oxide solutions affinity for carbonate, it is likely that carbonate constitutes a major proportion of the extracted salt. We can draw this conclusion because we have already found that vanadium is stripped from the organic phase by contacting with sodium carbonate solution, i.e., carbonate is preferentially extracted by phosphine oxide solutions.

III.B.2. Determination of the Percentage of Anthraquinone Disulfonic Acid Extracted from the Stretford Liquor by Trioctyl Phosphine Oxide Solution

In the Stretford solution the anthraquinone disulfonic acid species present varies with the degree of oxidation of the liquor. For the fully oxidized liquor it is present as the quinone, while in the reduced liquor it is present as the hydroquinone. If it were possible to determine either of the two sulfonic acid species present in solution, it would be possible to correlate this with the concentration of one of the vanadium species. This would then serve as a check for the vanadium(5) analysis.

Colorimetric analysis of the Stretford liquor for total anthraquinone disulfonic acid gave an optical density of 0.31 ± 0.02. Analysis of extracted liquor under the same conditions gave an optical density of 0.33 ± 0.03. It was concluded from these results that no anthraquinone disulfonic acid was extracted by trioctyl phosphine oxide solutions. This result is not unreasonable in light of the observations in Section II.B.1. and in particular Fig. 8. If we perform the corresponding charge/ionic mass calculation for anthraquinone disulfonic acid we arrive at a value of 0.0055. This is lower than any point on the graph (Fig. 8). Then from our previous conclusions (see Section II.B.1.) we could predict that no anthraquinone disulfonic acid would be extracted, a fact verified by the experimental result.

III.B.3. Extraction of a Reduced Stretford Liquor

Bubbling of the hydrogen sulfide through the Stretford liquor caused

Table 8

Percentage of Salts Extracted from the Stretford Liquor

Total dissolved salts in Stretford liquor

before extraction = 450 g/ℓ ± 2g/ℓ

Total after extraction by fresh phosphine oxide solution	% of total salts removed
383 g/ℓ ± 2.0 g/ℓ	14.8
388 g/ℓ ± 2.0 g/ℓ	13.8
382 g/ℓ ± 2.0 g/ℓ	15.1
391 g/ℓ ± 2.0 g/ℓ	12.9

Fig. 15. Flow Chart Of Salts Extracted From Stretford Liquor By Tryoctyl Phosphine Oxide Solution.

Composition of Stretford Liquor

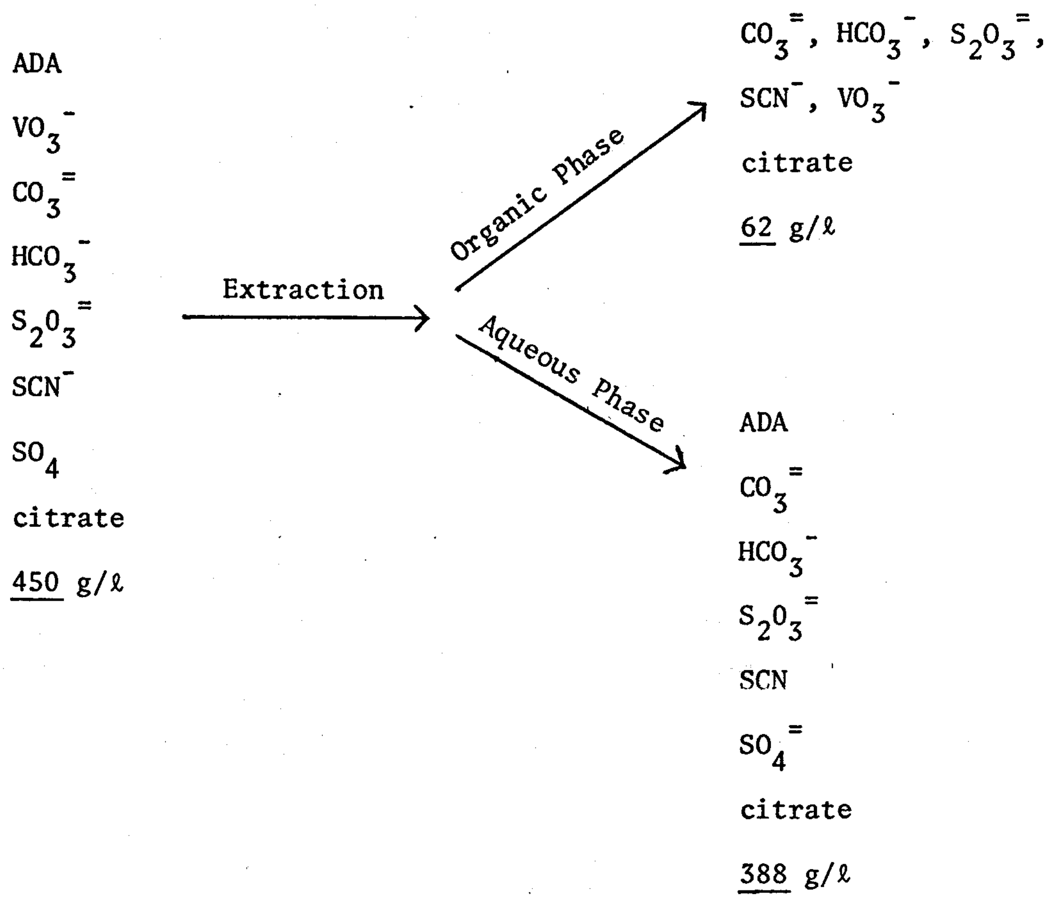


Table 9

Percentage V^5 in Reduced Liquor

% V in Organic Phase	% V in Aqueous Phase	Mass Balance	% V^5 in Reduced Liquor	% V^4 in Reduced Liquor
12.4±5.0 (abs.)	89.2±5.5 (abs.)	101.6±7.0 (abs.)	27.6±5.0 (abs.)	72.4±5.0 (abs.)
14.4±5.0	82.1±5.5	99.5±7.0	32.1±5.0	67.9±5.0
13.6±5.0	90.5±5.5	104.1±7.0	30.2±5.0	69.8±5.0
15.0±5.0	89.0±5.5	104.0±7.0	33.4±5.0	66.6±5.0

precipitation of a black solid, due to sulfide overloading of the liquor. This has been shown to be a vanadyl-vanadate of non-stoichiometric composition(9,10). As a consequence of this precipitate formation the total vanadium concentration dropped from 0.77 g/l to 0.53 g/l of sodium meta vanadate.

By using the vanadium(5) extraction coefficient found in Section III.B.1. it is possible to calculate the percentage of vanadium(5) present in the reduced plant liquor. This calculation is valid only if the vanadium(5) extraction coefficient is independent of

(a) the vanadium(4) concentration, and

(b) the vanadium(5) concentration.

Since it has been shown in Section II.B.3. that the vanadium(5) extraction coefficient is not dependent on either of these over the concentration range studied we are justified in using a recovery coefficient of 0.45 for analysis of the reduced plant liquor. These results are shown in Table 9, and as expected the vanadium(5) concentration decreased. If the total vanadium concentration is known, then we can determine the vanadium(4) concentration by difference.

III.C. Summary

From the experimental results obtained in Section III.B.1. and III.B.2. we can draw a flow chart indicating the species extracted by trioctyl phosphine oxide solution from the Stretford liquor (see Fig. 15).

Extraction of oxidized Stretford liquor by trioctyl phosphine oxide solution yields a recovery coefficient of 0.45 ± 0.08 and since from our previous work we found that the vanadium(5) extraction coefficient is independent of either the vanadium(4) concentration or the vanadium(5) concentration analysis of any oxidized, reduced or partially oxidized liquor is possible.

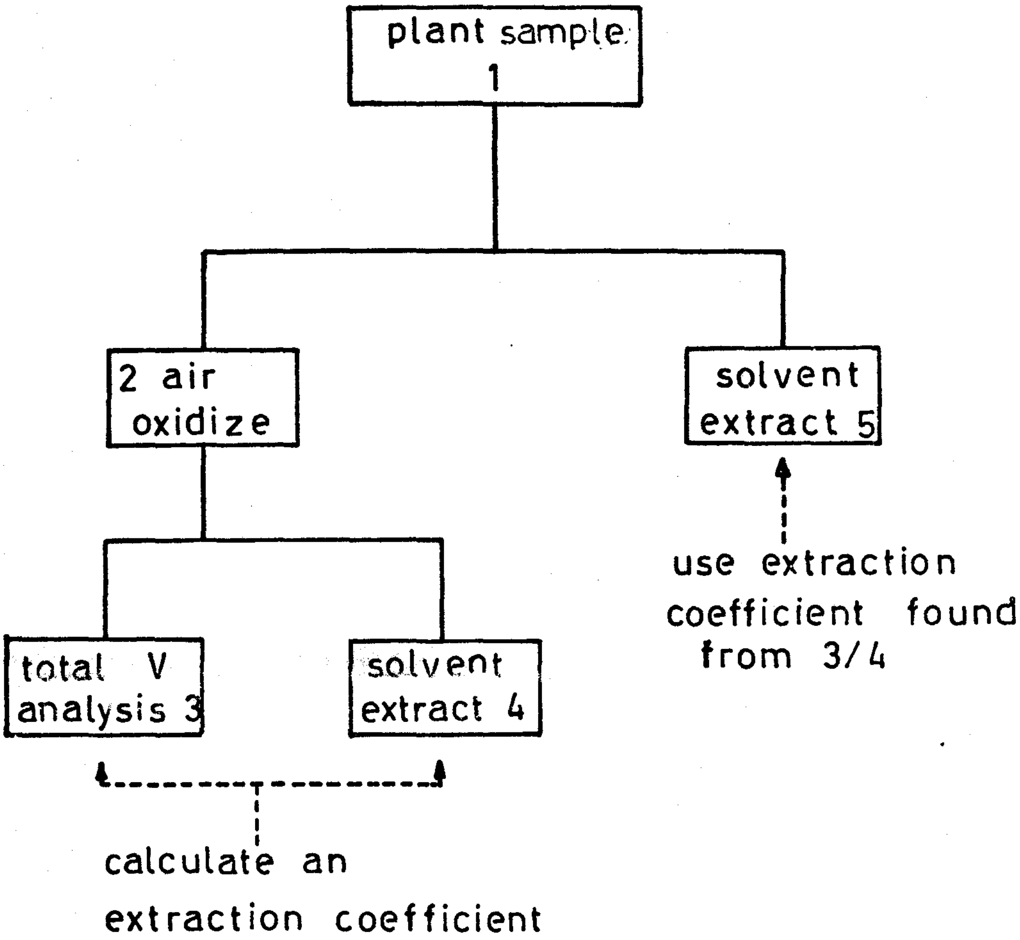
This developed procedure gives a method of analysis of the Stretford liquor for the ratio of vanadium(5)/vanadium(4). The recommended procedure is shown in flow chart form (see Fig. 16).

A knowledge of the vanadium(5)/vanadium(4) ratio is of prime importance in that it is a measure of the capacity of the plant to convert hydrogen sulfide from the gas stream to elemental sulfur. For example, if the ratio was high, this would indicate that the plant was not working to capacity, which is economically undesirable. A low ratio would tend to indicate that the plant was "flooded" with hydrogen sulfide from the gas stream and that appropriate steps be taken to either decrease the amount of gas adsorbed or to increase the capacity of the oxidizer.

Production of thiosulfate in the Stretford process is one of the undesirable side reactions because this adds to the total dissolved salts in solution. Eventually the dissolved salt concentration reaches such a high value that crystallization occurs within the system. It is then advantageous to the process to minimize the thiosulfate formation; this could be done by decreasing the time that the liquor spends in the oxidizer. A study of the vanadium(5)/vanadium(4) ratio in the oxidizer with time would give the shortest time necessary to fully convert all of the vanadium(4) to vanadium(5); this would then minimize the thiosulfate formed, and may prove to be economically advantageous in decreasing the operating costs of the plant.

Perhaps the greatest single disadvantage that the Stretford process has over other methods of gas purification is the disposal of "spent" plant

Fig. 16. Flow Chart Of Reccomended Procedure For Analysis Of Stretford Liquor.


plant sample 1
2 air oxidize
solvent extract 5
total V analysis 3
solvent extract 4
use extraction coefficient found from 3/4
calculate an extraction coefficient

liquor. It is occasionally necessary to replace old plant liquor with fresh material as the concentration of dissolved salts increases to the point of crystallization. The disposal of this discharged liquor is both difficult and expensive; difficult because of the environmental damage caused by large vanadium excesses, and expensive because of the cost of the vanadium catalyst, at present $4.00 lb.

Recovery of the vanadium catalyst then becomes essential if the Stretford process is to remain an important and economical method of gas purification. From our work on the analysis of the Stretford liquor we have seen it is possible to extract vanadium(5) from the liquor. It follows that this method of solvent extraction could be used to recover catalyst from spent liquor by the following steps:

1. Air oxidize the spent liquor.
2. Extract the oxidized liquor with trioctyl phosphine oxide solution.
3. Strip the phosphine oxide solution with sodium carbonate.

At stage 3 the aqueous phase contains vanadium, sodium carbonate and a small percentage (14.0%) of the dissolved salts from the Stretford liquor. It would only be necessary to add anthraquinone disulfonic acid and sodium citrate in order to use the solution in the Stretford process.

This solvent extraction method would effectively remove the vanadium from the spent liquor without bringing a high concentration of dissolved salts with it, and so enable us to reuse the catalyst. Disposal of Stretford solution that does not contain vanadium should prove to be easier than has been found in the past.

From our results the extraction of vanadium(5) from the Stretford liquor by trioctyl phosphine oxide solution we can then conclude the following:

1. that analysis of the Stretford liquor for the ratio of vanadium(5)/vanadium(4) is possible and desirable, to optimize plant conditions; and
2. that removal of the vanadium catalyst can be effected by our solvent extraction procedure.

IV. FUTURE WORK

By using the recommended method for analysis of the Stretford liquor it is possible to obtain the vanadium(5)/(4) ratio present in the plant at any time. If this ratio could then be correlated with the oxidation potential of the liquor it would be possible simply to measure the oxidation potential and by the calibration graph determine the vanadium(5)/(4) ratio.

The anthraquinone disulfonic acid exists as either the quinone, or the hydroquinone and these two forms may have different adsorption characteristics on alumina. If this is so it would be possible to separate the two forms by alumina chromatography, and so quantitatively determine the concentrations of each in the liquor.

Further investigation into analysis of the Stretford liquor for the oxidized and reduced anthraquinone disulfonic acid is worthwhile because this compound is one key to the understanding of the Stretford process.

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APPENDIX I. PREPARATION OF PHOSPHINE OXIDES

The phosphine oxides were prepared by the reaction of a grignard reagent with phosphorous oxychloride(28).

$$RBr + Mg \xrightarrow{ET_2O} RMgBr \qquad [1]$$

$$3RMgBr + POCl_3 \longrightarrow R_3P{=}O + 3MgBrCl \qquad [2]$$

Reagents

Magnesium - Shawinigan reagent.

Ether - Mallenckrodt anhydrous.

Alkyl Bromides - 1 bromo butane (B.D.H. reagent).

1 bromo hexane (Matheson, Coleman and Bell).

1 bromo octane (Eastman Organic Chemicals).

1 bromo decane (Eastman Organic Chemicals).

1 bromopentadecane (Eastman Organic Chemicals).

Phosphorous Oxychloride - Baker "analyzed" reagent.

The magnesium and dry ether were placed in a flask equipped with a condenser and dropping funnel; this was then stirred by means of a magnetic stirrer.

The alkyl bromide was placed in the dropping funnel and approximately 5 ml added to the ether-magnesium mixture without stirring. Once the mixture began refluxing it was then stirred, and the alkyl bromide added at such a rate as to maintain the reflux. After all the alkyl bromide had been added, the mixture was stirred to effect complete dissolution of the magnesium. At this point the phosphoryl chloride was continuously added at a rate to keep the mixture refluxing. The addition of phosphoryl caused the evolution of large quantities of heat, and it was occasionally necessary to cool the mixture. When all of the phosphoryl chloride had been added the mixture was poured onto ice water and stirred. The ether layer was withdrawn, and poured on to a solution of 0.05 M HCl, and again stirred for 2 hours. The etherial layer was withdrawn, washed twice with water, and the ether evaporated. The phosphine oxide was then used without further purification.

Those phosphine oxides deemed unsuitable for further studies were: (1) tributyl phosphine oxide; this was insoluble in kerosene. (2) tripentadecane phosphine oxide; owing to the high molecular weight of this compound it was not soluble to a concentration of 0.5 M.

APPENDIX 2. COMPOSITION OF BUFFER SOLUTIONS

All buffer solutions used in this study were carbonate/bicarbonate mixtures of the following composition.

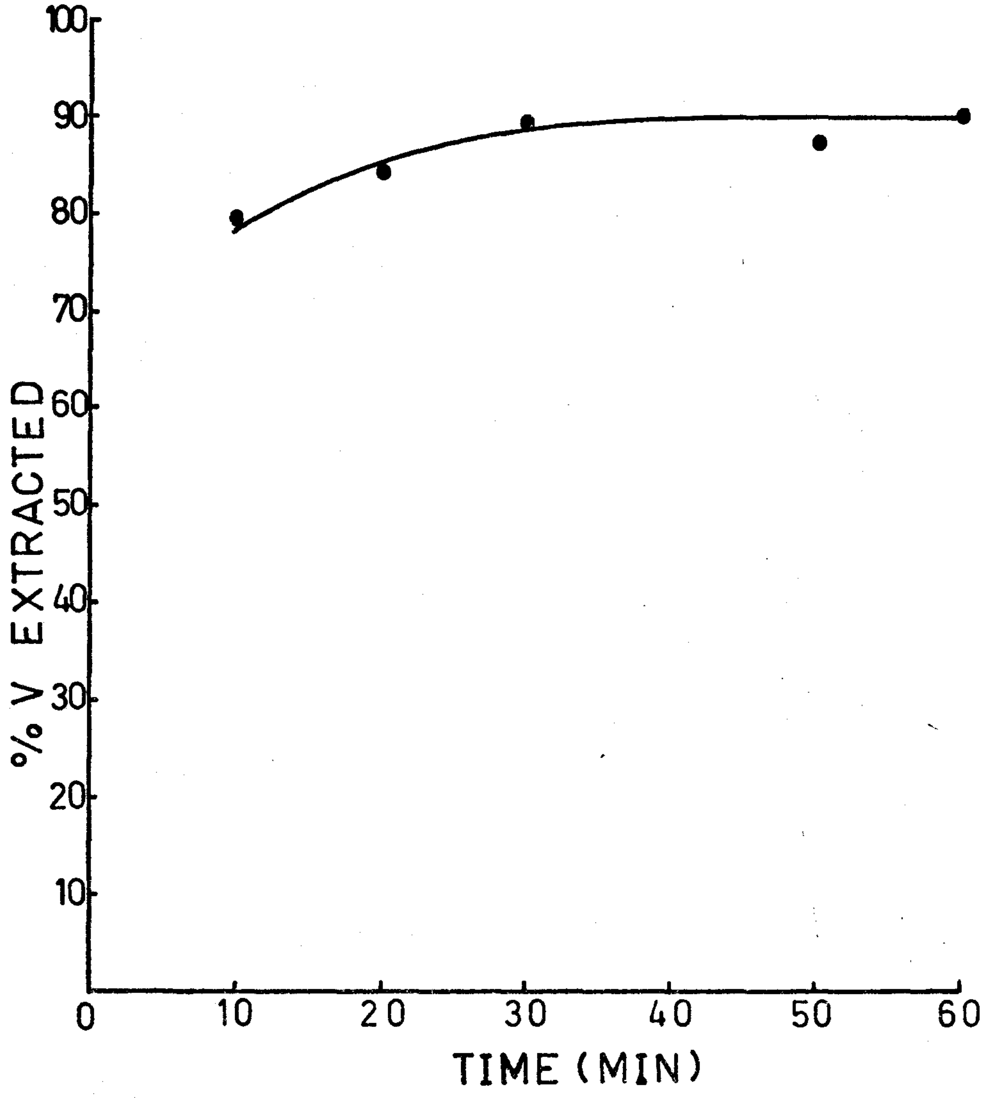
pH	ml of 0.1 M carbonate	ml of 0.1 M bicarbonate
9.16	1	9
9.4	2	8
9.51	3	7
9.78	4	6
9.9	5	5
10.14	6	4
10.28	7	3
10.53	8	2
10.83	9	1

For solutions of pH less than 9.16 a buffer of pH 9.9 was acidified with concentrated HCl to give the desired pH.

APPENDIX 3. SHAKING TIME NECESSARY FOR EXTRACTION

Standard vanadium(5) solutions were shaken by means of a wrist action shaker for time periods ranging from 10 min to 60 min with a solution of 0.5 M trioctyl phosphine oxide. Analysis of the aqueous solutions for vanadium(5) was then performed as usual (see Section II.A.3.a.). The percentage of vanadium(5) extracted by the phosphine oxide was then plotted as a function of time (see Fig. 17). From Fig. 17 we see that the maximum vanadium(5) extraction coefficient is reached after 30 min of shaking.

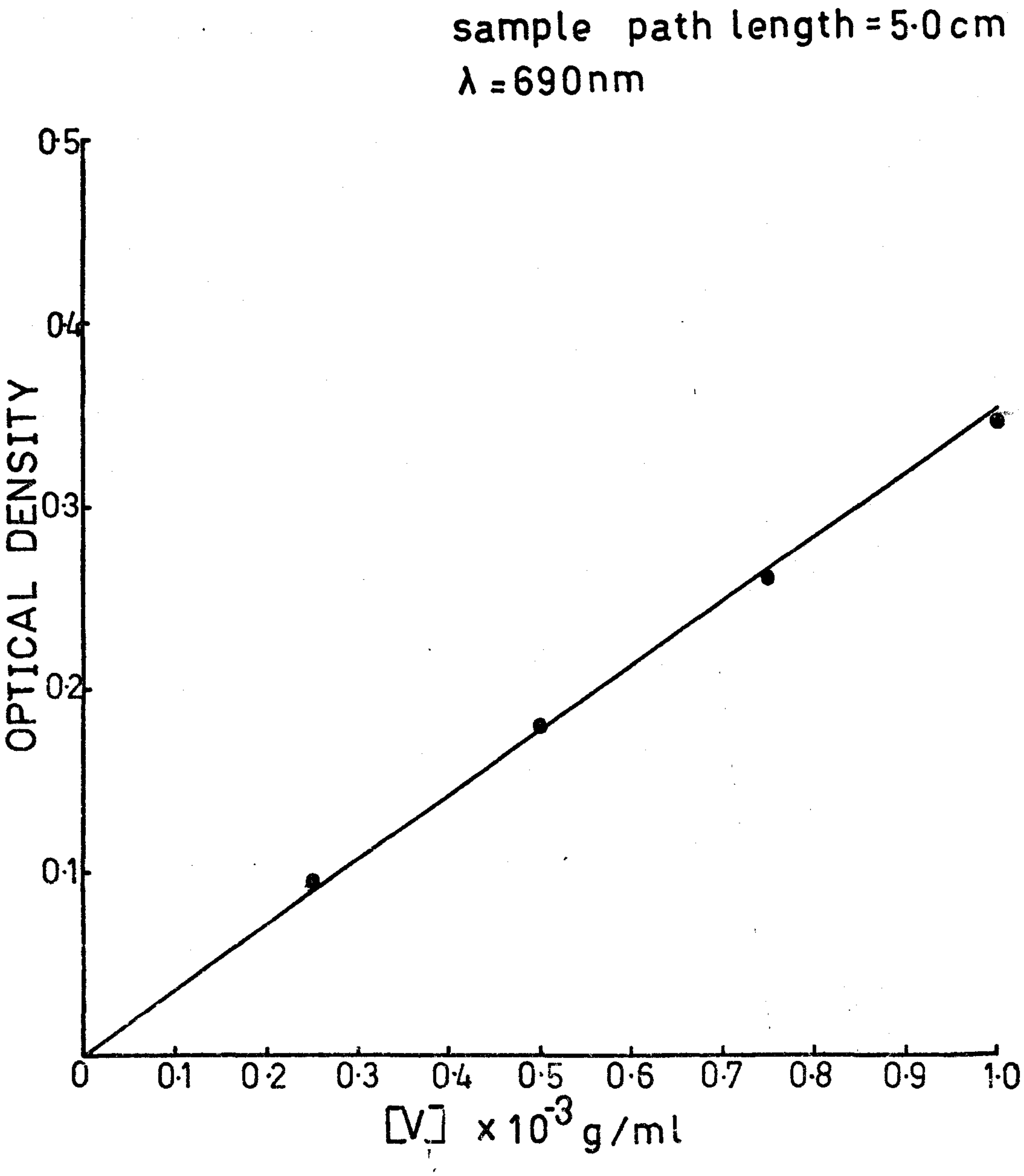
Fig. 17. Plot Of Percentage Of Vanadium (5) Extracted With Length Of Shaking.


100
90
80
70
60
50
40
30
20
10
0
10
20
30
40
50
60
% V EXTRACTED
TIME (MIN)

APPENDIX 4. BEER'S LAW PLOT FOR VANADIUM(5) SOLUTIONS

Standard vanadium(5) solutions were prepared by dissolving sodium meta vanadate in the appropriate pH 9.1 buffer. Aliquots of this vanadium(5) solution were then pipetted into beakers. These solutions were evaporated to dryness on a hot plate. The resulting precipitates were then dissolved in 20 ml of 1 M HCl, and 5 g of a silver amalgam added. The blue vanadium(4) colour was allowed to develop, and the optical density of these solutions read, using a sample pathlength of 5 cm at a wavelength of 690 nm. Fig. 18 shows the Beer's law plot obtained.

Fig. 18 Beer's Law Plot For Vanidium (5)


sample path length = 5·0 cm
λ = 690 nm
OPTICAL DENSITY
0·5
0·4
0·3
0·2
0·1
0
0·1
0·2
0·3
0·4
0·5
0·6
0·7
0·8
0·9
1·0
[V] x 10-3 g/ml