

T-1855

SEPARATION OF NITROGEN COMPOUNDS
FROM COAL LIQUIDS

By

Shahrokh Ghaffari Neyzari

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A Thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Master of Science in Chemistry.

Signed: S. Shaffer
Student

Golden, Colorado

Date: June 16, 1976

Approved: SRD
Thesis Advisor

George H. Kennedy
Head of Department

Golden, Colorado

Date: June 22, 1976

ABSTRACT

The purpose of the study was the development of a method of separation of the nitrogen compounds from coal liquids using ligand exchange chromatography. The sample used for this study was high volatile "C" bituminous coal from the Pittsburgh #8 Seam Ireland Mine, West Virginia, which had been converted to coal liquid by a CO-steam process.

Experimentation consisted of:

- A. Measurement of the total amount of nitrogen in the coal.
- B. Measurement of the total amount of nitrogen in the coal liquid.
- C. Determination of the percentage of nitrogen in those compounds which dissolve in methanol, the solvent selected for chromatogram development.
- D. Determination of the fraction of nitrogen which was absorbed on a column of sulfonate polystyrene resin which was loaded with copper (II) in methanol solution.

Two methods were used for preparing the ligand exchange columns:

- A. The resin was loaded with CuSO_4 in aqueous ammonia.
- B. The resin was loaded with CuCl_2 in methanol.

The results of separation by the two methods show that the columns which were packed with type (B) resin absorbed more nitrogen compounds than type (A). The eluant was methanol saturated with ammonia in both cases.

TABLE OF CONTENTS

	<u>Page</u>
Table of Figures	v
Acknowledgments	vi
Introduction	1
Experimentation	6
Sample Preparation	6
Reagent	6
Column	7
Resin	7
Preparation of Resin	7
Procedures for the Nitrogen Compound Separations	8
Calculation	11
Discussion	17
Literature Cited	22

TABLE OF FIGURES

	<u>Page</u>
Figure 1: Digestion apparatus	9
Figure 2: Distillation apparatus	10

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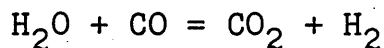
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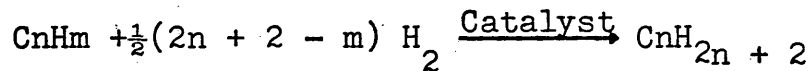
INTRODUCTION

Because of the energy shortage, pollution controls and undesirable dependence on foreign petroleum sources, there is today renewed interest in coal hydroliquefaction, to produce a clean fuel from domestic resources.

The co-steam process which has been used for converting coal to coal liquid, uses the water gas shift reaction,¹



to produce hydrogen for hydrogenation. The unsaturated compounds and nitrogen compounds are reduced to saturates and amines respectively.²



The methods which are used for separation of nitrogen compounds from liquid fuels are: The use of ferric chloride to form coordination complexes with nitrogen compounds in petroleum,³ and an improvement of this technique by supporting the metal salt on a kaolin substrate.⁴

A combination of the above techniques has been used to separate neutral nitrogen fractions from heavy-end petroleum distillates.⁵

Ion exchange chromatography has been used by Snyder and Buell to remove the nitrogen compounds from gasoline, by

using a bed of Duolite C-10 in the hydrogen form, previously equilibrated with methanol.⁶

The term "ligand exchange" was introduced in 1961 by Helfferich, to describe the exchange of electron-donating ligands (Lewis bases) coordinated to metal ions held by cation exchange resin.⁷

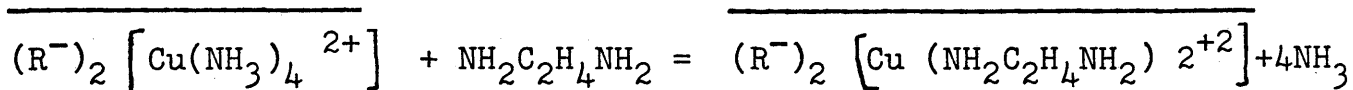
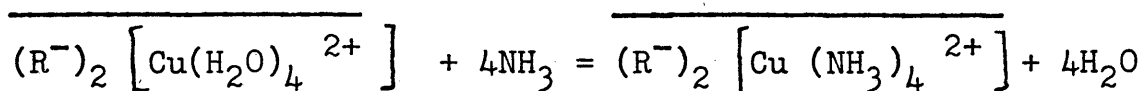
Ligand sorption by cation exchangers containing complexing metal ions was observed as early as 1954 by Walton.⁸

The method combines two fields of chemistry, namely, ion exchange and coordination chemistry, in order to accomplish a task that neither could do alone. An ion exchanger containing a complexing metal ion (Cu^{+2} , Co^{+3} , Ni^{+2} , Ag^{+} , etc.) is used as a solid sorbent. The potential ligands are sorbed from solutions or gases and form complexes with the metal in the resin by displacing other ligands which previously complexed the metal.⁷ Ligands which have been isolated or separated include ammonia, organic amines, polyhydric alcohols, olefins, acetylene derivatives, anions of organic acids and amino acids.

Ligand exchange has several advantages over conventional cation exchange. First, complex formation is a very strong interaction if the proper metal ion is chosen. This provides a very strong "driving force" for ligand sorption. Complexes of a metal ion with various, even-rather-similar ligands

differ greatly in their strength. Secondly, many variations of selectivity can be attained by changing the nature of the metal ion and the exchanger. Finally, the capacity of the resin is substantially increased, two fixed sulphonate ions bind one Cu^{+2} ion, which in turn can bind up to four amine molecules.⁹

Typical "ligand exchange" reactions are:⁹





where R represents the fixed ionic group of a cation exchanger, bars over symbols refer to the interior of the resin.

Ligand exchange chromatography has been very successful in separation of amines. Most ligand exchange studies of amines have been made with sulfonated polystyrene resins containing nickel ions. Helfferich⁷, used cation exchange resins loaded with the ions Cu^{+2} and Ni^{+2} in the form of their amine complexes to absorb the diamine 1,3-diaminopropan-2-ol from a dilute aqueous solution which also contained ammonia.

The following elution order has been observed for aliphatic amines¹⁰⁻¹¹ (the most weakly bound amine being listed

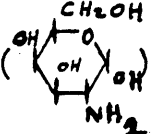
first) R_3N , R_2NH , RNH_2 . There is no correlation with strength of the amines as Bronsted-Lowry bases. The more highly branched the carbon chain, the more weakly the amine is held.

Ethylenediamine ($NH_2C_2H_4NH_2$), and 1,2- propanediamine are very strongly held; next 1,3- propanediamine, 1,6-hexanediamine and 1,4- butanediamine are less strongly bound.¹² It has been observed that hydrazine (H_2N-NH_2) itself is much more strongly held than its derivatives, monomethylhydrazine and 1,1- dimethylhydrazine.¹⁰ Also ethyleneimine ($\begin{matrix} H_2C-CH_2 \\ | \\ NH \end{matrix}$) is more strongly held than C - methylethyleneimine, and N - hydroxyethyleneimine is hardly bound at all.¹⁰

The following elution order has been observed for purine () and pyrimidine () bases, thymine, cytosine, adenine, and guanine.¹⁰

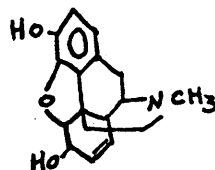
Amino acids ($R - \begin{matrix} CHCO_2^- \\ | \\ NH_3^+ \end{matrix}$) have been successfully separated by ligand exchange chromatography.¹³

Amphetamine ($C_6H_5CH_2CH_2NH_2$), phenethylamine, and related compounds have been separated on columns of cation-exchange resins loaded with ions of copper, nickel and cadmium.^{14,15}

Experiments have shown that the aminohexoses, glucosamine, galactosamine () and mannosamine are strongly held

on cation-exchange resin loaded by Ni^{+2} or Cu^{+2} ,¹⁵

Alkaloids (Morphine



) are separated

on resins having functional carboxyl groups combined with copper (II) ions.¹⁰⁻¹⁵

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EXPERIMENTATION

Sample Preparation

To obtain a homogeneous sample, the coal liquid was shaken for about one hour and divided into small bottles. These samples were not subdivided in later analyses.

Reagent

Anhydrous, analytical reagent grade methanol (Mallinckrodt Chemical Works Co.) was used.

Solutions of copper chloride in methanol were made by stirring (at ambient temperatures) anhydrous copper chloride (reagent grade, Baker and Adamson Co.) in methanol for a few minutes until the solution became saturated. The ammonical copper (II) sulfate solution was prepared by passing ammonia gas at a low flow rate through aqueous copper (II) sulfate (anhydrous, reagent grade, Baker and Adamson Co.) solution for one half hour until the solution became dark blue in color.

These reagents were used in the Kjeldahl-Gunning process. potassium sulfate, mercury (II) sulfate, selenium, granular zinc, all reagent grade.

Alkali solution was prepared from 100 g of potassium sulfide and 400 g of sodium hydroxide dissolved in distilled water and diluted to one liter with distilled water.

Methyl red indicator solution was prepared by dissolving 0.1 g of methyl red in 50 ml of methyl alcohol and adding 50 ml of distilled water.

Sodium hydroxide: 0.1 to 0.2 normal standard solution. Sodium hydroxide solution was standardized against 0.1 normal sulfuric acid.

Sulfuric acid: 0.2 normal.

Column

A glass buret (60 cm, 0.63 cm ID) was used as column.

Resin

Amberlite, CG-120, 200-400 mesh, 8% cross-linked, sulfonate polystyrene type resin ($\text{Na}^+ \text{RSO}_3^-$), was used as cation exchanger.

Preparation of Resin

The resin was treated in one of two ways to replace Na^+ with Cu^{+2} :

Type (A): The resin was stirred for about ten minutes with ammonical copper (II) sulfate solution and then washed with ammonical methanol solution, until the washings were colorless. The resin was placed into the burette and washed with 300 ml of methanol.

Type (B): The resin was stirred for about ten minutes in a solution of copper (II) chloride dissolved in methanol. The resin was then washed with methanol until a silver nitrate test with washings did not indicate the presence of chloride. The resin was loaded into a column and the packed column was washed with 300 ml of methanol.

Procedures for the Nitrogen Compound Separations

The experimental work included three stages. In the first, the percentage of nitrogen in coal and coal liquid was determined by the Kjeldahl-Gunning method as follows:¹⁷ One to two grams of the sample were weighed into a 500-ml boiling flask. For each gram of the sample, 6.5 g of potassium sulfate, 1.0 g of mercuric sulfate, 0.2 g of selenium, and 35 ml of sulfuric acid (reagent) were added to the flask. The contents of the flask were swirled to ensure thorough mixing and wetting of the sample. The digestion apparatus was arranged as shown in Fig. 1.

The contents were heated to boiling (the heat input was controlled in such manner that the sulfuric acid vapors condensed no more than halfway up the condenser). The boiling was continued until all the sample was oxidized, as evidenced by a nearly colorless solution.

When the digestion was complete and the solution had

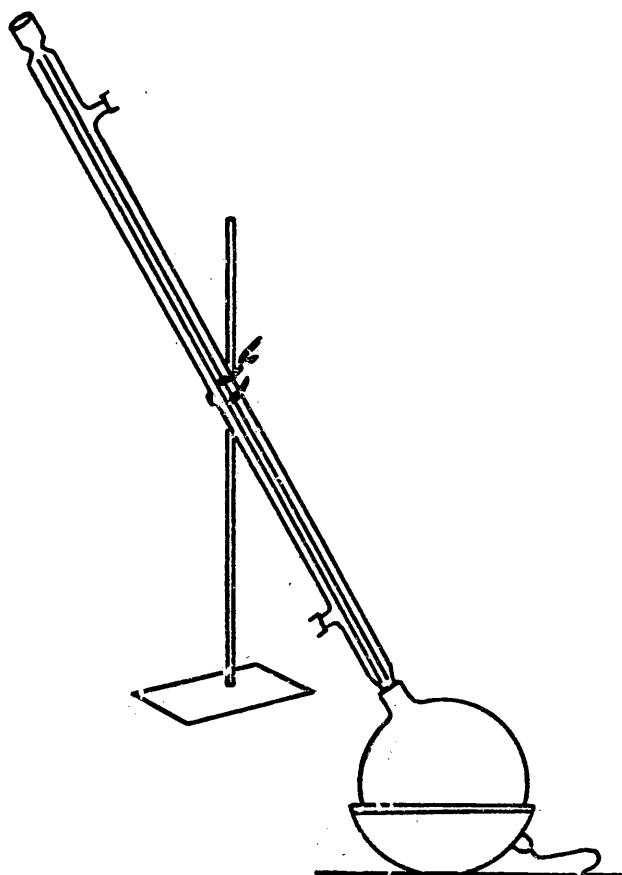


Fig. 1 Digestion apparatus

been cooled, a few crystals of potassium permanganate were added to ensure complete oxidation. The solution was heated to destroy the excess permanganate and decolorize the solution.

The cooled digestion mixture was diluted to about 300 ml with distilled water, and cooled in a water bath, to remove

the heat of dilution.

20.0 ml of (0.2N) sulfuric acid were measured into a 250-ml Erlenmyer flask and a few drops of methyl red were added. The flask was attached to a condenser with the outlet tube of the adapter submerged to maximum depth in the acid.

One to two grams of granular zinc were added to the mixture in the digestion flask and 120 ml of the alkali solution for each 35 ml of sulfuric acid was added very slowly so that it formed a distinct layer under the acid solution.

The flask was connected quickly to the distilling condenser as shown in Fig. 2.

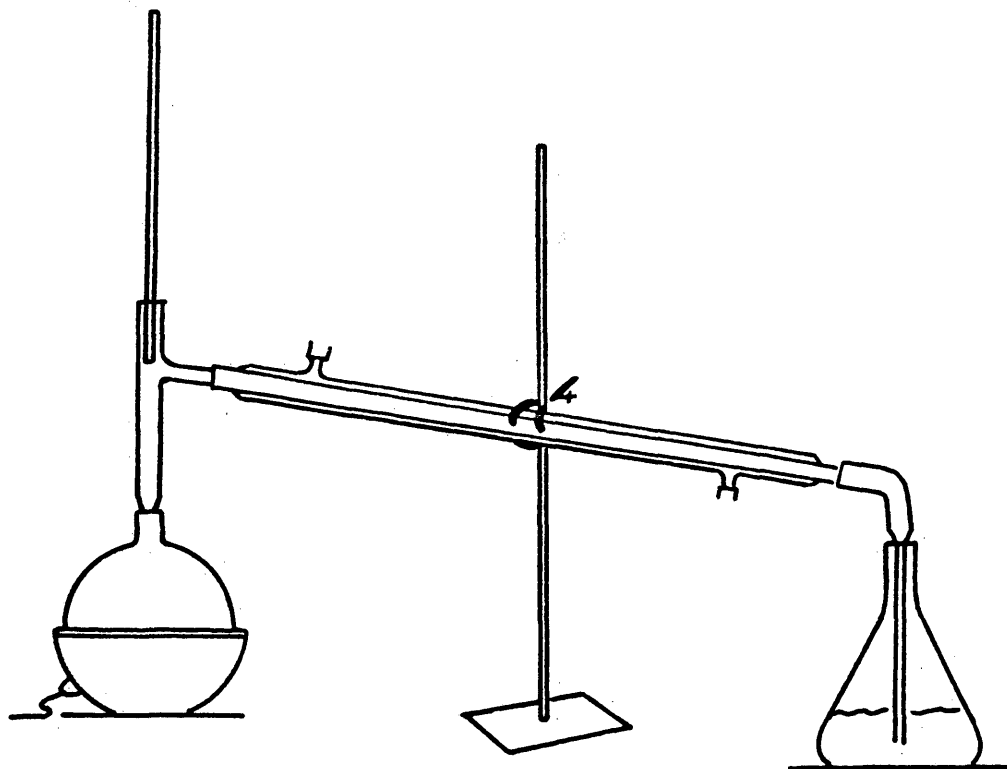


Fig. 2 Distillation apparatus

The contents were brought carefully to boiling. After collecting 100 ml of distillate, the Erlenmyer flask was removed. The condenser and adapter were rinsed with distilled water. These washings were combined with the distillate. The excess acid was then titrated with standard sodium hydroxide. A blank determination was made in the same manner to correct for nitrogen from sources other than the sample. Sucrose was used for blank determinations.

A blank determination was made whenever a new batch of any reagent was used in the analysis.

Calculation

The percentage of nitrogen in the samples was calculated as follows: The equivalent of sulfuric acid was calculated from the amount of NaOH which was used for titration.

B = milliliters of standard solution of sodium hydroxide required for titration of the blank.

A = milliliters of standard solution of sodium hydroxide required for titration of the sample.

N = normality of the sodium hydroxide solution.

C = grams of the sample used.



equivalents of acid titrated with NaOH in blank determinations:

$$\frac{(\text{B ml of NaOH}) \left(\text{N} \frac{\text{equiv. of NaOH}}{\text{lit of NaOH}} \right)}{\left(1000 \frac{\text{ml of NaOH}}{\text{lit of NaOH}} \right)} \cdot \frac{\text{equiv of H}_2\text{SO}_4}{\text{equiv of NaOH}}$$

$$= \frac{\text{B} \cdot \text{N}}{1000} \quad (\text{a})$$

equivalents of acid titrated with NaOH in sample determination:

$$\frac{(\text{A ml of NaOH}) \left(\text{N} \frac{\text{equiv of NaOH}}{\text{lit of NaOH}} \right)}{\left(1000 \frac{\text{ml NaOH}}{\text{lit NaOH}} \right)} \cdot \frac{\text{equiv of H}_2\text{SO}_4}{\text{equiv of NaOH}}$$

$$= \frac{\text{A} \cdot \text{N}}{1000} \quad (\text{b})$$

The difference between (a) and (b) is the equivalents of acid which is neutralized by NH_3 :

$$\frac{\text{B} \cdot \text{N}}{1000} - \frac{\text{A} \cdot \text{N}}{1000} + \frac{(\text{B} - \text{A}) \cdot \text{N}}{1000}$$

$$\text{gram nitrogen} = \frac{\text{H}_2\text{SO}_4 + 2\text{NH}_3 \longrightarrow (\text{NH}_4)_2\text{SO}_4}{\frac{(\text{B} - \text{A}) \cdot \text{N}}{1000} \cdot \frac{\text{equiv of NH}_3}{\text{equiv of H}_2\text{SO}_4}}$$

$$14 \frac{\text{gr of nitrogen}}{\text{equiv of NH}_3} = (\text{B} - \text{A}) \cdot \text{N} \cdot 0.0.4$$

$$\text{Nitrogen \%} = \frac{(\text{B} - \text{A}) \cdot \text{N} \cdot 0.0.4}{c} \times 100$$

The results of these determinations are shown in Tables (I) and (II).

Table I

Percentage of Nitrogen in Coal

<u>Run No.</u>	<u>g Sample</u>	<u>% Nitrogen</u>
1	0.4681	0.95
2	0.4790	1.03

Average % = 0.99

(0.95% N reported by Department of Chemical and Petroleum Refining Engineering.¹)

Table II

Percentage of Nitrogen in Coal-Liquid

<u>Run No.</u>	<u>g Sample</u>	<u>% Nitrogen</u>
1	1.7140	0.506
2	1.3313	0.493
3	1.2668	0.512
4	1.2103	0.482
5	1.8894	0.492

Average % = 0.497 ± 0.012

Methanol was chosen as the solvent to dissolve the compounds which contain nitrogen (amines) and to develop the chromatogram. For the purpose of determination of the

solubility of the nitrogen compounds in methanol, a few grams of sample (coal liquid) were weighed into an Erlenmyer flask and then methanol was added. The contents of the flask were shaken and after two or three days the contents of the flask were filtered (with paper filter) into a tared 500-ml boiling flask. The methanol was removed under vacuum in a desiccator. The boiling flask and contents were weighed. The difference of two weighings gave the weight of materials in flask.

The amount of the reagents needed for Kjeldahl-Gunning process were calculated from these weights. The solutions from runs No. 6, 7, 8 and 9 after filtering were divided in two parts. The first parts were used for measuring the percentage of nitrogen. The results are in Table III.

The second parts of No. 6 and 7 were subjected to ligand exchange in columns of type A, and No. 8 and 9 in columns of type B.

The first fraction was collected into a 500-ml boiling flask by passing methanol through the column to remove those compounds which were not absorbed by the resin. About 300 ml of methanol was used. Then ammonical methanol solution was passed through the column. This fraction was collected into a 500-ml boiling flask. The solvent was removed under vacuum

Table IIIPercentage of Nitrogen Dissolved in Methanol

<u>Run No.</u>	<u>g Sample</u>	<u>Ml MeOH Per g Sample</u>	<u>% Nitrogen Diss*</u>
1	1.004	40	65.40
2	1.0410	50	64.60
3	2.7103	90	65.60
4	2.6444	100	64.00
5	3.1878	100	66.00
6	2.2185	100	67.00
7	3.4493	100	66.60
8	2.2340	100	65.60
9	2.9390	85	65.20

Average % = 65.44 ± 0.93

*%Nitrogen dissolved calculation is based on average % of nitrogen in sample.

in a desiccator.

The amount of nitrogen in these fractions was measured by Kjeldahl-Gunning method.

The data from columns type A are shown in Table IV, and columns of type B in Table V.

Table IVThe Data From Column Type A

<u>Run No.</u>	<u>% Nitrogen Eluted by MeOH</u>	<u>% Nitrogen Eluted by NH₃/MeOH</u>	<u>% N Lost</u>
6	82.2	14.5	+ 3.3
7	82.6	13.2	+ 4.2

Table VThe Data From Column Type B

<u>Run No.</u>	<u>% Nitrogen Eluted by MeOH</u>	<u>% Nitrogen Eluted by NH₃ in MeOH</u>	<u>% N Lost</u>
8	55.5	49.7	- 5.2
9	56.5	47.8	- 4.3

DISCUSSION

According to data from the determination of the nitrogen in the coal and coal liquid shown in Tables I and II, the percentage of the nitrogen in the coal liquid is reduced to about 0.5 percent compared to 1.0 percent in the coal. Because the amount of coal which is used in liquefaction is not comparable to the amount of the coal liquid which is produced, the percentage of the nitrogen in the coal cannot be directly compared to the percentage of the nitrogen in the coal liquid. There is some loss of nitrogen as NH_3 gas during the hydrogenation process; however, the magnitude of this decrease is not defined by the analyses.

Methanol was chosen as chromatographic solvent because of its high polarity. Proper operation of the ligand exchange resin requires efficient solvation of the active resin sites.

As the data in Table III show, about 65 percent of the nitrogen is soluble in methanol. Data on the recovery of the coal liquid from coal indicate that about 80 percent of the coal is converted to coal liquid.¹ Methanol is not a good solvent for coal; only about 10 percent of coal is soluble in alcohol.¹⁸ An attempt to dissolve 0.5 gram coal in 50 ml methanol resulted in undetectable amounts of coal in solution. Therefore some of the loss may be in the form of unreacted coal. Further, some of the nitrogen compounds in the coal liquid may

have polynuclear structure and thus not be soluble in methanol. The results clearly show that some nitrogen compounds undergo ligand exchange and are retained on the column. The percentage of the nitrogen which is absorbed by the ligand exchanger is very different for the two types of resin. Indeed Type B absorbs about three times the nitrogen absorbed by Type A. Ligand exchange on Type A resins requires displacement of an ammonia molecule from its coordination site on the Cu(II) ion. With type B resins, ligand exchange requires displacement of a solvent (methanol) molecule from the coordination site. Since ammonia forms much stronger complexes with Cu(II) than does CH₃OH, weakly coordinating ligands may be unable to exchange on Type A resins but be able to do so on the Type B resins.

Separate 50 ml fractions of the NH₃/MeOH eluant from the ligand-exchange column were collected. Exploratory gas chromatographic analysis of each fraction showed a small number of peaks (less than ten). No compounds were found in the first fraction. The number of peaks (as determined by retention time) was found to increase in the second and third fractions and then decrease to zero in the fourth and fifth fractions. Therefore some separation of individual compounds on the ligand-exchange column was indicated.

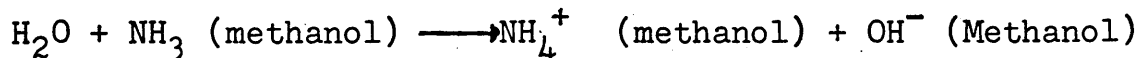
The possibility that some sulfur compounds were also absorbed on the resin was considered. Sulfur analysis of the

eluant indicated no sulfur in the fractions. The data in Table V show that type B resins absorb only about 50 percent of the nitrogen. This might be due to presence of nitrogen compounds of insufficient Lewis basicity to behave as ligands toward Cu(II). Some aromatic amines and some amides may fall in this category.

There is no data on the amount of recovery of nitrogen in liquid fuels by other methods³⁻⁴⁻⁵⁻⁶ to allow comparison of recovery efficiency.

The type A resin does have one advantage over type B. After elution, the resin is returned to its original form and is ready for another separation without further treatment. On the other hand, on continued use the concentration of metal ions on the resin decreases.¹⁰

Another problem which might arise with type A resins is the presence of water in the resin due to incomplete displacement of H₂O by NH₃. Ammonium ion may be formed by the process:



The resulting ammonium ion would be expected to displace Cu(II) from the resin by normal ion exchange.¹⁰ This problem could possibly be avoided by dissolving the copper (II) sulfate in methanol instead of H₂O.

The fourth column of Table IV shows a loss of about four percent of the total nitrogen in the process. It is possible that some of the nitrogen compounds remain in the column, not being eluted by solvent. However, these amounts correspond to rather small absolute quantities and may reflect the limit of the reproducibility of the analytical method.

In Table V, column four, the data show about 4.5 percent more nitrogen than the total nitrogen initially present in the coal liquid. The most probable cause is the presence of free Cu(II) ions in the column, which would form stable complexes ($\text{Cu}(\text{NH}_3)_4 \text{Cl}_2$) with ammonia molecules and Cl^- present in column.

These complexes are eluted by solvent into the fraction which is collected and increase the amount of nitrogen in the fraction.

The coal liquids contain about two percent iron.¹⁹ Fe(II) ions could displace Cu(II) ions on the resin and free the Cu(II) ions. Determination of Cu(II) in the eluant by atomic absorption indicated significant loss of Cu(II) from the column.

Other metal ions present in the coal liquid, which can form stable complexes with ammonia, may cause the same problem.

For further use of ligand exchange chromatography for separation of the nitrogen compounds from coal liquid, some

suggestions can be made.

1. The use of metal ions other than Cu(II), such as Ni(II) or Co(III) should be studied.²⁰ Nickel ions, of those ions which form ammonia complexes, are most strongly bound to sulfonated polystyrene resins.¹⁰⁻¹⁵ Ni(II) ions have been more widely employed than other metal ions in ligand exchange chromatographic separation of amine compounds.
2. Cation exchange resins with carboxyl functional groups, show somewhat better metal retention than those with sulfonate functional groups.¹⁰⁻²¹ This advantage could decrease some of the error due to displacement of metal ions from the resin.
3. Solvents other than methanol should be investigated. Tetrahydrofuran (THF) has been shown to be a good solvent for the dissolution of coal liquids.

Experimentation demonstrated very high solubilities of coal liquids in tetrahydrofuran. Tetrahydrofuran, also, is a stronger Lewis base than methanol due to increased electron density on oxygen in tetrahydrofuran. Therefore tetrahydrofuran can form more stable complexes with metal ions like Cu(II), Ni(II) and etc.,²² than can methanol.

If complexed ligands were eluted by displacement by the solvent, tetrahydrofuran, molecules, then initial removal of non-basic components would be necessary.

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