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SEPARATION OF NITROGEN COMPOUNDS BY ACYLATION-CATION EXCHANGE

by

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ABSTRACT

A method for separation of nitrogen compounds from a solution has been studied. This method involves N-acylation with acetyl chloride in the presence of cation exchange resin in the sodium form. The interaction of the cation with the exchange resin functions to stabilize the cation and effect its separation from other constituents. The quantity of nitrogen compounds removed was determined by nitrogen analysis of the cation exchange resin. Several factors influence the separation: 1) ratio of quantity of sample to quantity of resin; 2) ratio of quantity of sample to quantity of acetyl chloride, and 3) contact time between resin and reactant system.

The method was used to separate quinoline from a solution containing quinoline and acetophenone in tetrahydrofuran (THF). Dimethylquinoline and aniline were removed from a dichloromethane solution also containing dodecane and naphthalene. Nitrogen compounds present in shale oil and coal liquids were partially removed.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

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INTRODUCTION

Natural Systems

The United States is involved in an energy problem. Domestic sources of petroleum are being depleted creating a dependence upon imported oil. The need for domestic liquid fuel has encouraged research on the conversion of coal, oil shale, tar sands and related fuel sources into liquid products. This is not the first time we have looked for alternate liquid feedstocks. In the early 1920's, fears of depleted petroleum feedstocks encouraged research in synthetic fuels. The discovery of vast petroleum reserves in Texas in the late 1920's ended this stage of research. The Germans used coal liquids to supply their army in World War II. Coal research was revived after the war, but slowed after the discovery of Middle East oil in the mid 1940's. The rapid rise in oil prices since the embargo of 1973 has increased the interest in synthetic fuels.

One problem with synthetic fuel is the high heteroatom content in comparison to petroleum. Nitrogen compounds pose a variety of problems:

1. The nitrogen compounds will act as catalyst poisons in the refining process.

2. If such fuels are to be upgraded, appropriate catalysts and conditions must be chosen to remove the nitrogen compounds.
3. The presence of nitrogen compounds can adversely affect the storage characteristics of finished fuel products.
4. Some nitrogen compounds have been shown to be carcinogenic and mutagenic; thus they represent a danger to workers in the synthetic fuel industry.

Currently the nitrogen compounds are removed by hydroprocessing or hydrodenitrification (HDN) reactions (1). HDN is postulated to be a three step process for heterocyclics: 1) hydrogenation of the aromatic and heterocyclic ring, 2) slow rupture of the ring at the C-N bond, 3) rapid denitrogenation to paraffins and ammonia. This process is kinetically controlled by the second step. To reduce residence times the process is typically run at 400°C and 1500 psig of hydrogen (1). The HDN reactions are carried out over expensive catalysts (Ni-Mo, Co-Mo, Ni-W) with lives of over 200 hrs (2). The high temperature and pressure, hydrogen demand and expensive catalyst render this an expensive refining method. This cost has encouraged researchers to investigate alternate means to reduce the heteroatom content of the synthetic fuels before processing. These studies will furnish information about the chemistry of nitrogen compounds typically found in synthetic fuels.

McKay and his co-workers (3) removed nitrogen compounds from crude oil by eluting a petroleum distillate through a cation exchange resin in the hydrogen form. The acid portion of the distillate had been removed previously. This is an acid extraction method. The base fractions of the distillate are protonated by the acidic cation exchange resin; the resulting cations then occupy the exchange sites. This method will remove not only nitrogen compounds, but all basic components in the distillate. Some weak nitrogen bases are not removed from the distillate because the extent to which they are protonated by the acidic resin is small.

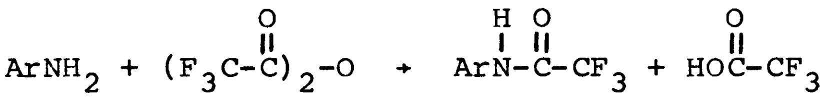
Thompkins (4) has also used an acid extraction to separate bases. He extracted several different synthetic liquids with 6M HCl. The aqueous fraction was neutralized with base and the organic compound removed by ether extraction.

Hartung and Jewell (5) removed nitrogen compounds from a furnace oil by the direct addition of metal salts to the sample liquids. The nitrogen compounds and metal ions interacted in a Lewis acid-base reaction. The nitrogen compounds acted as Lewis bases and coordinated to the metal ion as Lewis acid. The salts with coordinated nitrogen compounds were removed by filtration. Testing of the furnace oil before and after addition of metal salt showed a reduction in nitrogen content. A problem with this procedure is the possibility that some metal salts will dissolve in the oil and not be removed by filtration. Shue and Yen (6) attempted to correct this problem by adsorbing the metal salt, $FeCl_3$, on clay. They eluted a shale oil through the clay and removed 60% of the nitrogen compounds. They also found that a portion of the $FeCl_3$ was desorbed from the clay and found in the product fractions. The $FeCl_3$ had to be removed using a cation exchange resin.

Helfferich (7) removed amines with a cation-exchange resin in a metal ion form. A cation-exchange resin is converted to a metal ion form by equilibrating the resin with a concentrated solution of the metal ion. The displaced protons are removed by repeated rinsing of the resin with solvent. A solution of nitrogen bases is added to the resin where they replace ligands present on the metal ion (generally solvent molecules). Walton (8) has done extensive work documenting this process (ligand exchange chromatography). He has shown that the quantity and type of nitrogen compounds retained on the resin are dependent upon the strength of the complex formed between the ligand and the metal ion.

Adsorption chromatography has been used to isolate a nitrogen-rich fraction (9,10,11). The procedure of Shiller (9), separates nitrogen compounds on an alumina column. This procedure makes use of solubility differences of components of a coal-derived liquid. The sample is added to the top of an alumina column which is eluted with a sequence of solvents: hexane, toluene, chloroform. The nitrogen compounds were found to elute as a dark band in the chloroform fraction.

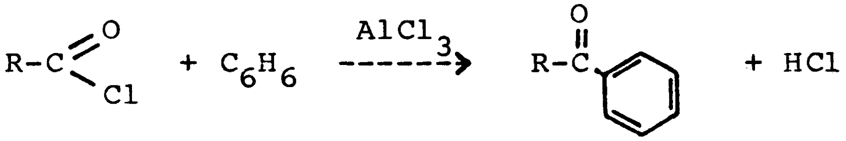
Several workers (12,13,14) have formed derivatives of nitrogen compounds and then analyzed for the derivatization product. Trifluoroacetic anhydride reacts with aromatic amines to form trifluoroacetamides.



$$\mathrm{ArNH_2} + (\mathrm{F_3C}\text{-}\overset{\overset{O}{\|}}{\mathrm{C}})_2\text{-}\mathrm{O} \rightarrow \mathrm{Ar}\overset{\overset{H}{|}}{\mathrm{N}}\text{-}\overset{\overset{O}{\|}}{\mathrm{C}}\text{-}\mathrm{CF_3} + \mathrm{HO}\overset{\overset{O}{\|}}{\mathrm{C}}\text{-}\mathrm{CF_3}$$

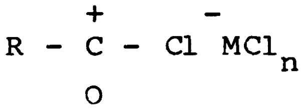
GC/MS data is used to identify and quantify these derivatization products. This reaction is based on nucleophilic attack by the amine group on the electrophilic carbonyl center in trifluoroacetic anhydride.

The term acylation refers to the addition of an acyl group, RC = O (where R = alkyl or aryl) to a compound to form a new carbon-carbon bond. An example of this reaction is the formation of a phenyl ketone depicted below:



This reaction is referred to as a Friedel-Crafts acylation. Historically, acylation at carbon sites has been used in the synthesis of ketones. C. Friedel and J.M. Crafts reported the formation of benzophenone from benzoyl chloride and benzene in the presence of aluminum chloride in 1877 (15). Acylation reactions can also occur at nucleophilic sites other than ring carbon such as oxygen or nitrogen nonbonding pairs.

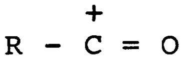
The acylating reagent (usually an acid halide or anhydride, but sometimes an acid or ester) is electrophilic. Catalysts for these reactions polarize the acylating agent to increase the electrophilicity of the acyl carbon. Two possible forms of the acylating reagent are depicted below (16):



$$R - \underset{O}{\overset{+}{C}} - Cl\ \overset{-}{M}Cl_n$$

(I)

or

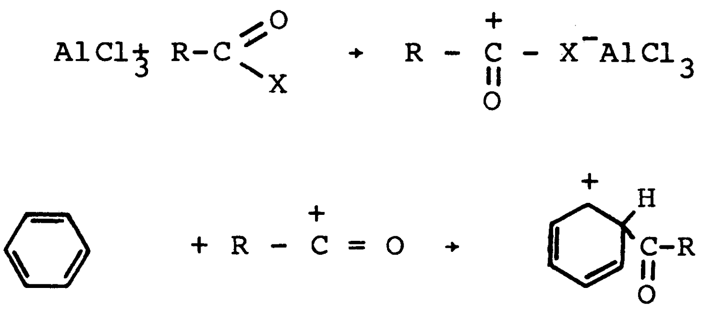


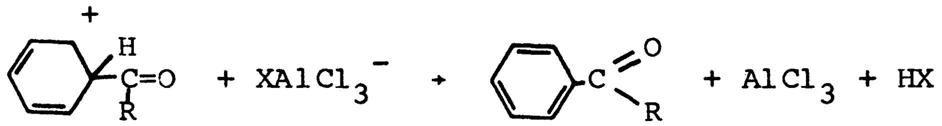
$$R - \overset{+}{C} = O$$

(II)

Species I is a complexed acylium ion. (It has an ion pair where the catalyst MCl_n is associated with the acylating agent.) Species II is a free acylium ion.

The participation of both the complexed and free acylium ions in a Friedel-Crafts acylation has been reported. Conductance measurements of a solution of aluminum chloride in benzoyl chloride indicate a slight dissociation of the complex into free ions; while benzoyl chloride and molten gallium chloride give a conducting medium where the ionization is extensive (16). High resolution proton and fluorine magnetic resonance studies indicate the presence of acylium salts, $RCO^+ \; MF_4^-$ in a mixture of acetyl, propionyl, and benzoyl fluorides with SbF_5, AsF_5, PF_5 and BF_3 (17). It is likely that both species occur in acylating mixtures, with the predominant form determined by the nature of the solvent. The ion pair forms first; then dissociates into separate ions in appropriate solvents. The mechanism of the Friedel-Crafts reaction may be written:



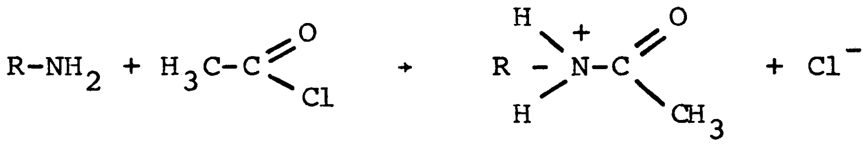


Unsubstituted aromatic hydrocarbons can be acylated in reasonable yields with suitable catalysts (17,18). The mechanism for ring acylation has as an intermediate step, the formation of a sigma complex between the acyl carbon and the carbon in the aromatic ring. The sigma complex intermediate is of high energy because the formation of the sigma bond involves an electron pair localized from the aromatic π system. The loss of the π delocalization energy thus represents a large increment of activation energy for the process. Consequently, acylation without a catalyst proceeds slowly. The keto group introduced in Friedel-Crafts ring acylations is an electron-withdrawing substituent. The electron-withdrawing groups further destabilize the sigma complex; so acylation usually does not proceed beyond monoacylation unless sufficient electron-donating substituents (i.e. alkyl groups) are present on the ring (17). Toluene reacts with acetic anhydride in the presence of Lewis acid catalyst in 70% yield. By contrast benzene reacts with acetic anhydride in the presence of the same catalyst to give only 30% yield of the ketone (19).

Nitrogen Acylation

A competing reaction to aromatic ring acylation is nitrogen or oxygen acylation. Nitrogen or oxygen acylation will proceed at a greater rate than aromatic ring acylation when the nitrogen or oxygen has a pair of electrons that is not involved in a π system. These electrons will be used in the formation of a sigma bond between the heteroatom and the acyl carbon without accompanying loss of delocalization energy. This reduces the activation energy compared to ring acylation; therefore the reaction proceeds at a greater rate.

Ring acylation of primary and secondary aromatic amines is usually not satisfactory since the acylating agent may attack preferentially at the nitrogen site (17). Acylation of the aniline ring proceeds only after nitrogen acylation. For example, if the acylating agent is acetyl chloride, nucleophilic substitution for chloride yields:

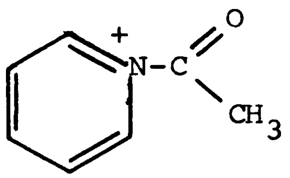


$$R\text{-}NH_2 + H_3C\text{-}C(=O)Cl \rightarrow R\text{-}\overset{+}{N}H_2\text{-}C(=O)CH_3 + Cl^-$$

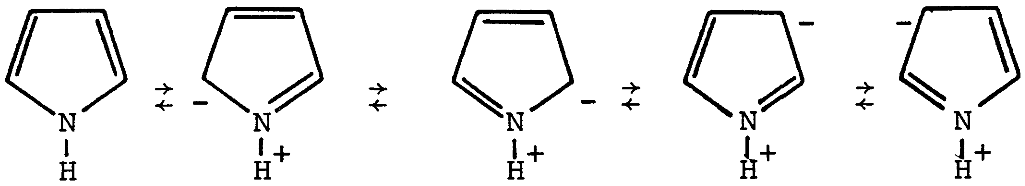
The cation formed deprotonates to form the N-acylated compound, R-$NHCOCH_3$.

Analogous N-acylation occurs with both unsaturated and saturated heterocyclic compounds and the corresponding alicyclic compounds. The nitrogen reacts by nucleophilic attack on acylating agents, thus resembling the mechanism for amines. When the heterocyclic ring contains a system of conjugated double bonds, two types of reaction behavior are observed. Pyridine and pyrrole are examples of compounds that illustrate the two different reactions.

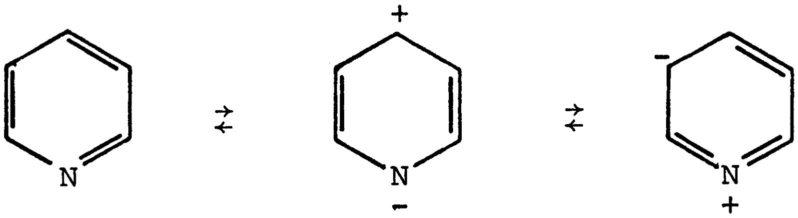
Pyridine and quinoline have fully aromatic ring systems. Both rings have six π electrons (one being donated by nitrogen) in delocalized π orbitals. The sigma electrons are polarized due to the high electronegativity of nitrogen. This inductive effect of the nitrogen atom creates a dipole with the negative end at the nitrogen atom and the positive end at the center of the molecule (17,20). The effect of this decrease in electron density is analogous to that observed when an electron-withdrawing group, such as a nitro group, is present on a benzene ring. The nitro group deactivates the ring to electrophilic attack. Friedel-Crafts acylation is particularly difficult to accomplish on pyridine. The lack of reactivity is partly due to the lone pair of electrons on the nitrogen. The electrons may interact with the electrophile (nucleophilic attack) to form the cation depicted below (3,4).



Pyrrole (also carbazole, indolizines) has six pi electrons in delocalized orbitals. The nitrogen atom contributes two electrons to the pi system. The dipole is opposite that of pyridine with the positive end on the nitrogen atom and the negative end in the center of the molecule. The difference in dipole moments for pyridine and pyrrole is caused by two factors. The first is an inductive effect where the sigma electrons in both compounds are polarized toward the nitrogen atom by the greater electronegativity of nitrogen relative to carbon. The inductive effect is seen in both compounds. The second factor is the electron density of the pi-electrons. Pyrrole has the π electron density concentrated on the four carbon atoms as seen in the resonance structures following:

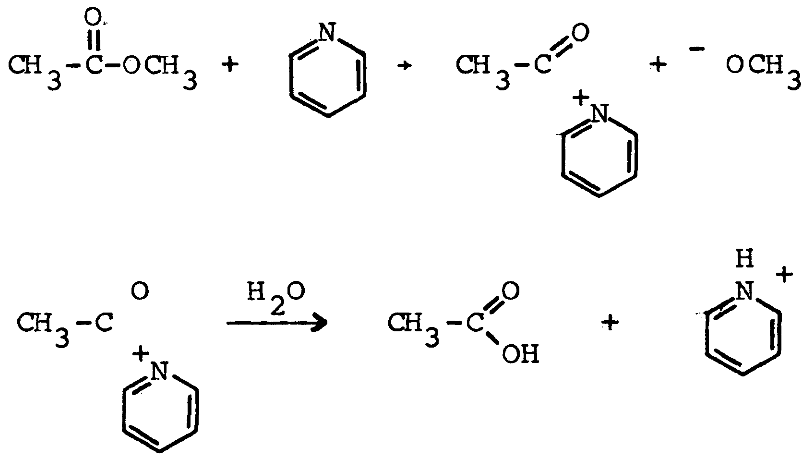


Pyridine has the π electron density more uniformly distributed over all the atoms in the compound as seen below:



Only the inductive effect operates in pyridine to create a dipole. In pyrrole, the resonance effect is greater than the inductive effect so there is a reversed dipole compared to pyridine. The increased electron density at the carbon atoms in pyrrole makes the compound susceptible to acylation. Pyrrole can be acylated with acetic anhydride without the aid of a catalyst (20). After acylation, the ring is deactivated to further acylation (17,20).

Nucleophilic reactions of nitrogen heterocyclics and carboxylic acid derivatives are documented (21,22,23). Pyridine has been used as a nucleophilic catalyst in ester hydrolysis. The first step in the hydrolysis is a reaction between the carbonyl of the ester and pyridine. The acetyl pyridinium ion thus produced was shown to be sufficiently long-lived to react with hydroxylamine in the presence of water (21). The acetylpyridinium ion can be observed spectrophotometrically (24,25). The mechanism (21) for the hydrolysis is:



Pyridine catalyzes the hydrolysis by nucleophilic displacement of the $^{-}OCH_3$ group to form the acetylpyridinium ion which is converted back to pyridine and a carboxylic acid in the presence of water. Both steps occur more rapidly than does direct displacement of $^{-}OCH_3$ by H_2O.

The reaction between acyl carbon and nitrogen compounds is dependent upon the nucleophilicity of the nitrogen. Nucleophilicity is a measure of the rate with which a nucleophile reacts with a reference electrophile. Strong nucleophiles react at a greater rate than weak nucleophiles. There are several factors that affect nucleophilicity (26): 1) the base strength of the compound, 2) the polarizibility of the nucleophilic atom, 3) the presence of unshared pairs of electrons on the atom adjacent to the nucleophilic atom, and 4) solvation effects.

The relationship between nucleophilicity and rate has been shown by Swain and his coworkers (27) to be logarithmic. There is no general correlation between basicity and nucleophilicity. Linear relationships between basicity and nucleophilicity have been reported for compounds of constant steric requirements (21).

This study proposes exploiting the reaction between nitrogen compounds and acylating species to remove the nitrogen compounds from a solution. This can be considered a Lewis acid-base reaction between an electron pair donor (nitrogen compounds) and an electron pair acceptor (a carbonyl carbon).

In the nucleophilic reaction, the nitrogen atoms donate a pair of electrons to a carbonyl carbon. The reaction has an intermediate step in the formation of a cation as in the case of the acetylpyridinium ion. The acylation of a tertiary amine has the cation as a final product, while secondary and primary amines deprotonate to form stable amides. The cation products usually revert back to reactants. In this study the feasibility of stabilizing the intermediate cation by replacement of the sodium on the exchange resin with the intermediate cation was investigated. The cation formed in the intermediate step will be placed in contact with a cation exchange resin in the sodium form. The procedure is based on N-acylation proceeding at a greater rate than corresponding acylation of saturates, unsaturates and aromatics. This type of preference can be predicted by Pearson's (28) hard and soft acid base theory. His theory predicts that hard acids (low polarizibility) will react preferentially with hard bases, while soft acids (high polarizibility) will react preferentially with soft bases. The nitrogen compounds (primary, secondary, heterocyclic) are harder bases than are saturates, unsaturates and aromatics. The hardness of acylating species is comparable to that of the nitrogen compounds. The saturates, unsaturates, and aromatics should react slowly or not at all with the acylating species without catalyst present (29).

The alternate approach to the separation involving protonation of the nitrogen compounds is less favorable since H^+ is harder than either the acyl carbon or nitrogen compounds. The nitrogen compounds would preferentially react with the acyl carbon because of the greater similarity in hardness of the two compounds.

Further information on acylation, nucleophilicity and reactions involving nitrogen compounds has been reported in the literature (30-36).

EXPERIMENTAL WORK

The experimental work for this study consisted of preparation of the cation exchange resin, acylation of samples in the presence of the resin, separation of resin and retained components from the sample solution, and analysis of both resin and depleted sample solution.

All the solvents and compounds used in this study were commercial "reagent grade" chemicals used without further preparation.

The cation exchange resins used were:

Dowex 50W-X4 - a sulfonic acid cation exchange resin in the hydrogen form

Capacity: 5.2 meq/dry gram
1.1 meq/ml resin bed
64-72% moisture by weight

Dowex HCRW-2 - a sulfonic acid cation exchange resin in the sodium form

Capacity: 2.0 meq/dry gram
1.9 meq/ml resin bed
47% moisture by weight

Dowex 50W-X8 - a sulfonic acid cation exchange resin in the sodium form

Capacity: 6.27 meq/dry gram
1.9 meq/ml resin bed
43% moisture

Resin Preparation

The cation exchange resin in the hydrogen form was first converted to the sodium form for these experiments. The resin was slurried with dry THF saturated with sodium chloride. This solution was agitated by hand for 1 minute and allowed to stand for 24 hours. Then the liquid solution was decanted and the resin rinsed 8 hours with THF in a Soxhlet extractor. The THF extraction was used to remove water from the resin. After extracting with THF the resin was stored as a slurry with THF in a sealed container.

The Dowex 50W-X8 and HCRW-2 resins in the sodium form were prepared by extracting the resin with THF to remove water. They were also stored as a slurry with THF in a sealed container. When dichloromethane was used as a solvent, the cation exchange resin was further rinsed with dichloromethane to remove the THF. It was stored as a slurry in dichloromethane in a sealed container.

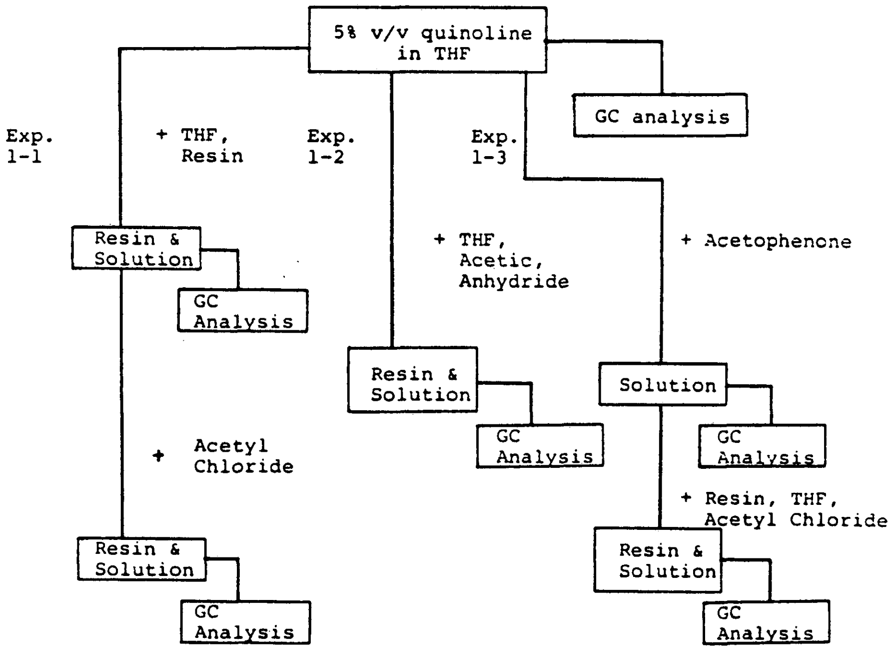
Procedures

All experiments were run in a batch mode in Pyrex containers. The experimental work was divided into three phases; 1) Phase One experiments were used to determine qualitatively if the process produces a separation. 2) Phase Two was used to obtain a mass balance and to determine quantitatively the influence of acetyl chloride concentration, quantity of resin, reaction time, and type of nitrogen compounds on the separation obtained. 3) in Phase Three the utility of the separation method was investigated by efforts to desorb the nitrogen compounds from the resin and experiments with syncrudes.

Phase One experiments were designed to determine if the separation method worked Experiment 1-1 was performed using a 5% (V/V) solution of quinoline and THF. A flow sheet for experiment 1-1 is seen in Figure 1. The quinoline solution was analyzed on a gas chromatograph (GC) and retention times for THF and quinoline determined. Ten ml of THF and 2 grams (on a dry basis) of Dowex 50W-X4 cation exchange resin converted to the sodium form were added to 5 ml of the quinoline-THF solution. The mixture was agitated by hand for one minute and allowed to stand for 30 minutes. A sample was removed from the solution and analyzed by GC. Five ml of acetyl chloride were added to the mixture, which was agi-

Figure 1

Flowsheet for Experiment 1-1, 1-2, and 1-3



tated briefly by hand and then allowed to stand for 30 minutes. A sample was removed from the solution and analyzed by GC.

Experiment 1-2 (see Figure 1) was performed using 5 ml aliquots of the same quinoline-THF solution used in experiment 1-1. Ten ml of THF, 2 grams (on a dry basis) of the Dowex 50W-X4 cation exchange resin converted to the sodium form, and 5 ml of acetic anhydride were added to the quinoline solution. The mixture was agitated briefly by hand and then allowed to stand for 30 minutes. A sample was removed from the solution and analyzed by GC.

Experiment 1-3 (see Figure 1) was performed using a 5 ml aliquot of the same quinoline solution used in experiment 1-1 and 5 ml of 5% (V/V) solution of acetophenone in THF. Five ml of THF, 2 grams (on a dry basis) of Dowex 50W-X4 cation exchange resin converted to the sodium form, and 5 ml of acetyl chloride were added to the quinoline/acetophenone solution. The mixture was agitated by hand briefly and then allowed to stand for 30 minutes. A sample was removed from the liquid solution and analyzed by GC.

Experiment 1-4 was a time study of the separation method. Five ml aliquots of the quinoline solution used in experiment 1-1 were placed in Pyrex containers. Ten ml of THF, 2 grams (on a dry basis) of the Dowex 50W-X4 cation exchange resin converted to the sodium form, and 5 ml of acetyl chloride were added to each aliquot. The three samples were agitated by hand briefly. A sample was removed from mixture 1 five minutes after the addition of acetyl chloride. A sample was removed from mixture 2 fifteen minutes after the addition of acetyl chloride. A sample was removed from mixture 3 thirty minutes after the addition of acetyl chloride. All samples were analyzed by GC.

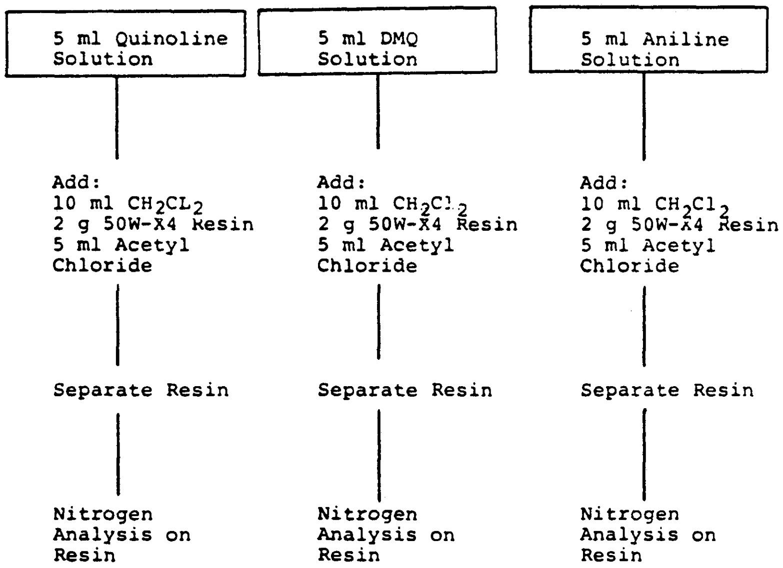
Phase 2 experiments were designed to investigate the operating parameters of the separation method to provide information for optimizing the separation. These experiments investigated the influence of different resins, quantity of resin, quantity of acetyl chloride, reaction time, mixtures of different compounds, and different nitrogen compounds on the separation. Mass balances were obtained.

Experiment 2-1 (see Figure 2) was a series of experiments designed to determine quantitatively if nitrogen compounds were being associated with the cation exchange resin during the separation method. Three solutions of nitrogen compounds were prepared:

1. 2.5 ml of quinoline diluted to 100 ml with dichloromethane.
2. 3.4 g 2,6-dimethylquinoline diluted to 100 ml with dichloromethane.

Figure 2

Flowsheet for Experiment 2-1



3. 2.0 ml aniline diluted to 100 ml with dichloromethane.

Experiment 2-1 was performed by preparing 3 mixtures each containing 10 ml dichloromethane and 2 grams (dry basis) of Dowex 50W-X4 cation exchange resin converted to the sodium form. Five ml of the quinoline solution was added to mixture 1, 5 ml of the dimethylquinoline solution was added to mixture 2, and 5 ml of the aniline solution was added to mixture 3. Five ml of acetyl chloride was added to each mixture; the mixture was agitated by hand, and then allowed to stand for 30 minutes. At the end of the thirty minutes, each solution was decanted, each resin was washed with 10 ml of dichloromethane, and each supernatant decanted off. Each resin was air dried and then analyzed for nitrogen content. The procedure above for quinoline was repeated with Dowex HCRW-2 cation exchange resin replacing the Dowex 50W-X4.

Experiments 2-2 and 2-3 were designed to investigate the effect on the separation achieved by the quantity of exchange resin added. Experiment 2-2 was done by preparing 5 mixtures containing 5 ml of the quinoline solution (2.5% V/V in CH_2Cl_2) from experiment 2-1, 10 ml of dichloromethane, and 5 ml of acetyl chloride. Then 0.7 g (dry basis) of the Dowex 50W-X4 cation exchange resin converted to the sodium form was added to mixture 1, 1.3 g to mixture 2, 3.4 g to mixture 3, 5.1 g to mixture 4, and 8.0 g to mixture 5. The mixtures were agitated by hand and allowed to stand for 30 minutes. After 30 minutes the solution was decanted off each resin; each resin was washed by decantation with 10 ml of dichloromethane. Each resin was air dried and then analyzed for nitrogen content.

Experiment 2-3 was performed with a solution of 3.4 g of 2,6 dimethylquinoline dissolved in sufficient dichloromethane to yield 100 ml of solution. Five mixtures were prepared containing 5 ml of the dimethylquinoline solution, 10 ml dichloromethane, and 5 ml of acetyl chloride. Then 0.3 g (dry basis) of Dowex HCRW-2 cation exchange resin was added to mixture 1, 1.0 g to mixture 2, 1.5 g to mixture 3, 2.6 g to mixture 4, and 5.5 g to mixture 5. The mixtures were agitated by hand and allowed to stand for thirty minutes. After the thirty minutes, the solution was decanted off each resin; each resin was washed by decantation with 10 ml of dichloromethane. Each resin was air dried and analyzed for nitrogen content.

Experiments 2-4 and 2-5 were designed to investigate the influence of acetyl chloride concentration on the nitrogen separation by this method. Experiment 2-4 was performed by preparing a mixture containing 5 ml of dimethylquinoline solution (3.4 g/100 ml), 10 ml dichloromethane, and 1.5 g of Dowex HCRW-2 cation exchange resin. One ml of acetyl chloride was added to mixture 1, 2.0 ml to mixture 2, 3.0 ml to mixture 3, 5.0 ml to mixture 4, and 10.0 ml to mixture 5. The mixtures were agitated by hand and allowed to stand for 30 minutes. After thirty minutes the solution was decanted off each resin; each resin was washed by decantation with 10 ml of dichloromethane. Each resin was air dried and analyzed for nitrogen content.

Experiment 2-5 was performed using the same dimethylquinoline solution as in experiment 2-4. Five mixtures were prepared containing 5 ml of the dimethylquinoline solution, 10 ml dichloromethane, and 3.0 g (dry basis) of the 50W-X8 cation exchange resin. Two ml of acetyl chloride was added to mixture 1, 1.0 ml to mixture 2, 0.8 ml to mixture 3, 0.3 ml to mixture 4 and no acetyl chloride was added to mixture 5. The mixtures were agitated by hand and allowed to stand for thirty minutes. The solutions were decanted from each resin into tared containers; each resin was washed with 10 ml of dichloromethane and the wash decanted into the same containers as the solution (depleted fraction). Each resin was air dried and analyzed for nitrogen content. Each solution plus wash sample was evaporated to dryness at ambient temperature. Each container plus residue was weighed, and each residue was analyzed for nitrogen content to obtain a mass balance.

Experiment 2-6 was carried out using the dimethylquinoline solution (3.4 g diluted to 100 ml in dichloromethane) from previous experiments. Four mixtures of 5 ml of the dimethylquinoline solution, 10 ml dichloromethane, and 5 g of the 50W-X8 cation exchange resin were prepared. Two ml of acetyl chloride were added to mixture 1; it was agitated by hand, and then allowed to stand for 5 minutes. At the end of five minutes the solution was decanted off the resin; and the resin was washed by decantation with 10 ml of dichloromethane. Two ml of acetyl chloride were added to mixture two, three, and four. They were agitated by hand. Mixture 2 was decanted after 15 minutes, mixture 3 after 30 minutes, and mixture 4 after 60 minutes. Each resin was separated by the same procedure used for mixture one. Each resin was air dried and analyzed for nitrogen content.

Experiment 2-7 was conducted using a solution of 1 g dimethylquinoline, 0.58 g aniline, 0.82 g naphthalene, and 1.08 g dodecane dissolved in dichloromethane to yield 100 ml solution. Three mixtures were prepared containing 5 ml of the mixture, 10 ml dichloromethane, 5 g Dowex 50W-X8 cation exchange resin, and 2 ml acetyl chloride. The mixtures were agitated by hand and then allowed to stand for 2 hours.

After 2 hours the liquid phase was decanted off each resin; each resin was washed by decantation with 10 ml of dichloromethane. A sample of the starting solution and sample from the three decantates were removed and analyzed by GC.

Phase Three experiments were designed to investigate the utility of the separation method. Experiment 3-1 was designed to determine if the nitrogen compounds associated with the cation exchange resin could be removed from the resin. Two mixtures were prepared containing 5 ml of a dimethylquinoline solution (3.4 g diluted to 100 ml with dichloromethane), 10 ml dichloromethane, 4 g of the Dowex 50W-X8 cation exchange resin, and 2 ml of acetyl chloride. The mixtures are agitated by hand and then allowed to stand for 2 hours. After two hours, the solutions were decanted into tared containers, and the resins were washed by decantation with 10 ml of dichloromethane. The washes were combined with the decantates in the same tared containers. Each liquid phase was evaporated to dryness at ambient temperature; and each residue was analyzed for nitrogen content. The resin from each mixture was placed in a separate container and 20 ml of absolute alcohol were added to each. The mixtures were agitated by hand, and then allowed to stand for 24 hours. After 24 hours the alcohol was decanted off the resin into tared containers; each resin was washed by decantation with 10 ml of alcohol. The wash was combined with the decantate. The alcohol was evaporated to dryness at room temperature; Each residue was analyzed for nitrogen content. The resin was air dried and analyzed for nitrogen content.

In experiment 3-2, two mixtures of dimethylquinoline, dichloromethane, Dowex 50W-X8 cation exchange resin, and acetyl chloride were prepared as in experiment 3-1. After decantation, 20 ml of a 10% (V/V) of concentrated HCl and water was added to each resin. The mixtures were agitated by hand and then allowed to stand for 24 hours. After 24 hours the liquid phase was decanted off; each resin was washed with 20 ml of water. Each resin was air dried. A portion of each resin was removed for nitrogen analysis. The remainder of each resin was mixed with 20 ml of a 1 N solution of NaOH. The mixture was agitated by hand and then allowed to stand for 24 hours. After 24 hours the liquid phase was decanted, and each resin was washed with 20 ml of water. Each resin was air dried and analysed for nitrogen content.

In experiment 3-3, syncrudes were used to evaluate the separation method. Experiment 3-3-1 was performed by preparing two mixtures, each containing 1.3 g of a raw Parahoe shale oil, 15 ml dichloromethane, 3 g Dowex 50W-X8 cation exchange resin and 3 ml acetyl chloride. Experiment 3-3-2 was identical to 3-3-1 with 2 g of a Utah syncrude used instead of the Parahoe shale oil. Experiment 3-3-3 was done using 3 g of a Kentucky syncrude instead of the Parahoe shale oil used in 3-3-1. All six mixtures were agitated by hand, and then allowed to stand for two hours. After two hours, the solution was decanted off each resin; each resin was washed twice by decantation with 20 ml of dichloromethane. Each resin was air dried and analyzed for nitrogen content.

Methods of Analysis

GC analyses were performed using a Varian Model 3700 gas chromatograph equipped with a FID detector and OV-17 column (3% on Chromasorb W-HP, 80/100) programmed for 130°C for 1 minute, rising at 15°C/min until 220°C was reached. Helium was used as the carrier gas at a rate of 20 ml/min.

Elemental analyses were performed by two labs. Part of the samples were analyzed by the Chemical and Petroleum Refining Engineering Department at the Colorado School of Mines. These samples were analyzed on a Carlo-Erba elemental analyzer. The remaining samples were analyzed by a commercial laboratory, Camp, Dresser, and McKee, 11455 West 48th Avenue, Wheatridge, Colorado 80033.

RESULTS AND DISCUSSION

Phase I

Experiments were designed to determine qualitatively if the separation method worked. The results of Experiments 1-1, 1-2, 1-3, and 1-4 are seen in Table 1.

The retention time for quinoline was determined from samples of the quinoline solution. When the quinoline and resin are mixed together the quinoline is detected in the solution by the GC (Figure 3). That quinoline remains in solution indicates that the resin does not remove quinoline from the solution at an appreciable rate.

When acetyl chloride (Figure 3) is added to the mixture, the solution phase is found to contain, by comparison to the retention time determined earlier, no quinoline (Figure 4). There are three possible explanations for this observation; 1) quinoline is converted to some species (presumably a cation) in the solution phase which does not pass through the GC column, 2) a substitution product is formed which has a different retention time than does quinoline, 3) a cation is formed which remains bound to the resin. No GC peaks corresponding to substitution products were observed although the column temperature was

Table 1

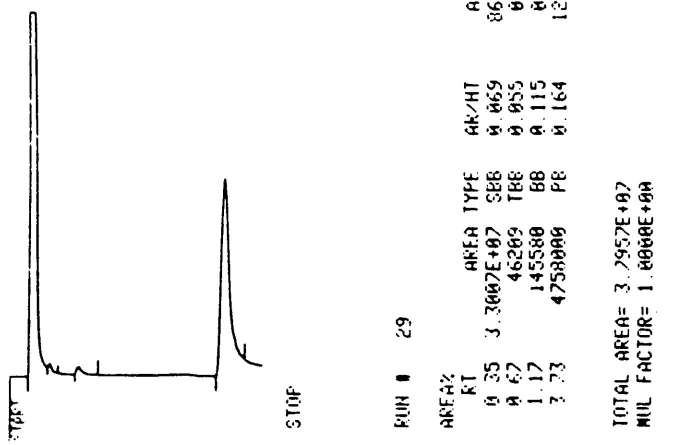
Phase I Experiments

Solvent: THF (10 ml)
Resin: Dowex 50W-X4 in Na^+ form
Quinoline Solution: 2.5 ml quinoline diluted to 100 ml with THF

Number	Components In System	Reaction Time	Components in the Solution Phase
1-1	Quinoline	0 min	Quinoline
1-1	Quinoline, Resin	30 min	Quinoline
1-1	Quinoline, Resin, Acetyl Chloride	30 min	Acetyl Chloride
1-2	Quinoline, Resin, Acetic Anhyride	30 min	Quinoline, Acetic Anhydride
1-3	Quinoline, Acetophenone, Acetyl Chloride	30 min	Acetophenone, Acetyl Chloride
1-4	Quinoline, Resin,	0 min	Quinoline
1-4	Quinoline, Resin, Acetyl Chloride	5 min	Acetyl Chloride
1-4	Quinoline, Resin, Acetyl Chloride	15 min	Acetyl Chloride
1-4	Quinoline, Resin, Acetyl Chloride	30 min	Acetyl Chloride

Figure 3

Gas Chromatograms for Experiment 1-1



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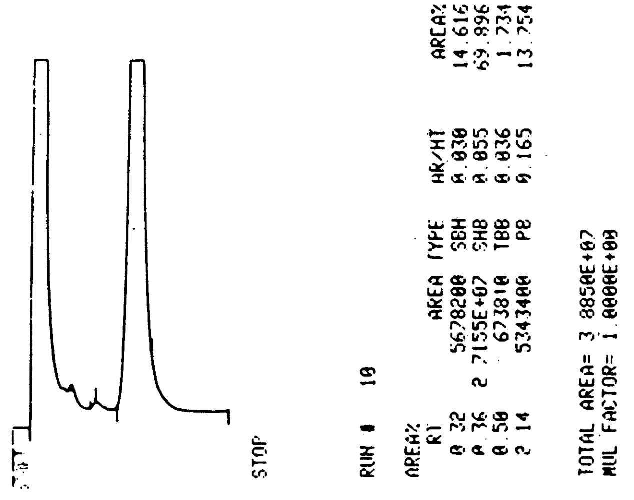
RUN #   29

AREA%
  RT          AREA TYPE   AR/HT       AREA%
 0.35  3.3007E+07  SBB   0.069      86.959
 0.62       46209  TBB   0.055       0.122
 1.17      145580   BB   0.115       0.384
 3.73     4758000   PB   0.164      12.535

TOTAL AREA= 3.2957E+07
MUL FACTOR= 1.0000E+00
```

A. GC of Quinoline in THF solution



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RUN #   10

AREA%
  RT          AREA TYPE   AR/HT       AREA%
 0.32     5678200  SBH   0.030      14.616
 0.36  2.7155E+07  SHB   0.055      69.896
 0.50      673810  TBB   0.036       1.734
 2.14     5343400   PB   0.165      13.754

TOTAL AREA= 3.8850E+07
MUL FACTOR= 1.0000E+00
```
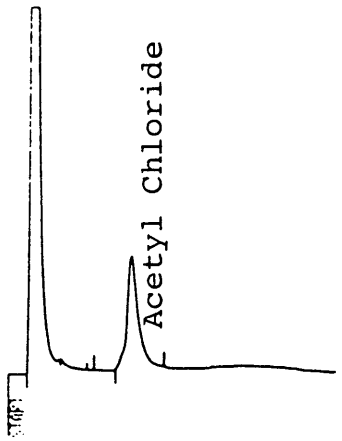

B. GC of Acetyl Chloride in THF solution

Figure 4

Gas Chromatograms for Experiments 1-1 and 1-3



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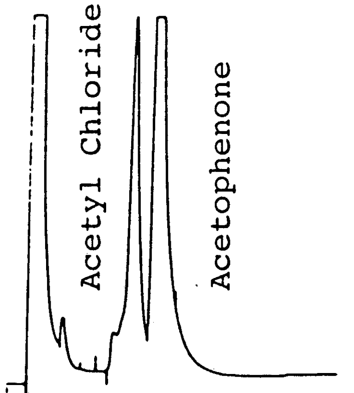
RUN #   15

AREA%
   RT            AREA TYPE    AR/HT        AREA%
  0.37  3.2808E+07 ↑SPB    0.066       97.317
  2.10       904660   PB    0.210        2.684

TOTAL AREA= 3.3712E+07
MUL FACTOR= 1.0000E+00
```

A. GC of supernatant of solution containing quinoline, acetyl chloride, resin, and THF



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RUN #   25

AREA%
   RT            AREA TYPE    AR/HT        AREA%
  0.37  3.6126E+07  SBB    0.076       90.997
  0.91        54616  TBB    0.089        0.138
  2.09      1085900   PP    0.171        2.735
  2.48      2433600   PB    0.149        6.130

TOTAL AREA= 3.9700E+07
MUL FACTOR= 1 0000E+00
```

B. GC of supernatant of solution containing quinoline, acetyl chloride, acetophenone, resin, and THF programmed to 220°C. The other two possiblities are more probable.

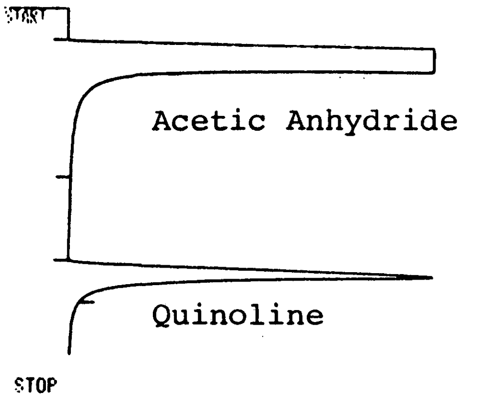
In experiment 1-2, acetic anhydride was added instead of acetyl chloride. Both acetic anhydride and quinoline were found in the solution phase (Figure 5). There was no apparent reduction in the quinoline concentration. This experiment indicates that acetyl chloride is superior to acetic anhydride for this separation. The reason for the superiority of the acetyl chloride is the nature of the leaving group. The chloride in acetyl chloride is a better leaving group than the acetate in acetic anhydride. Since chloride is a better leaving group the reaction between quinoline and acetyl chloride is more favorable than the reaction between quinoline and acetic anhydride.

In experiment 1-3, quinoline and acetophenone were separated. The GC analysis of the solution (Figure 4) indicated acetophenone but no quinoline in the solution. Therefore, quinoline is retained on the resin while acetophenone is not.

Experiment 1-4 was a time study of the retention of quinoline. Quinoline was detected in the solution phase by GC before the addition of acetyl chloride. Five minutes after the addition of acetyl chloride, quinoline was not detected in the solution. GC analysis of the solution at 15

Figure 5

Gas Chromatograms for Experiment 1-2



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RUN #   12

AREA%
  RT          AREA TYPE   AR/HT      AREA%
 0.66      1857600   PV   0.125      44.537
 0.91      2124300   VB   0.117      50.932
 4.54       188970   PB   0.219       4.531

TOTAL AREA=    4170900
MUL FACTOR= 1.0000E+00
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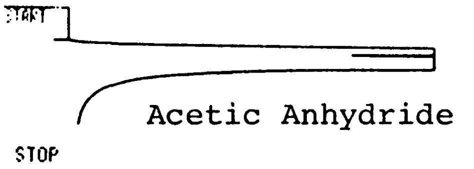

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RUN #   10

AREA%
  RT          AREA TYPE   AR/HT      AREA%
 0.69      457080   PV    0.068      10.138
 0.90     4051700   VB    0.134      89.862

TOTAL AREA=    4508700
MUL FACTOR= 1.0000E+00
```

and 30 minutes also produced no evidence of quinoline. Therefore, the processes responsible for removal of quinoline from the solution phase are completed within five minutes following the addition of acetyl chloride.

Phase II

These experiments were designed to provide information for optimizing the separation method. Experiments from Phase I showed that quinoline could be removed from a solution. The first part of Phase II was to show that quinoline and similar nitrogen compounds become associated with the resin. The results are seen in Table 2.

Under these conditions, a larger percentage of quinoline than of aniline or dimethylquinoline (DMQ) was removed by the 50W-X4 resin. The cation exchange resin manufactured in the sodium form (HCRW-2) also removed quinoline but not in as great a quantity as the resin that had been converted to the sodium form (50W-X4). One reason for the difference in recovery could be the difference in capacities of the two resins (50W-X4 = 5.2 meq/g versus HCRW-2 = 2.0 meq/g). The capacity of a cation exchange resin is a measure of the concentration of active sites on the resin. The active sites are sites where a sodium cation can be replaced by another cation. Since the 50W-X4 resin has a greater capa-

Table 2

Comparison of Different Nitrogen Compound Removal

Resin Type (2g added)	Nitrogen Compound	Grams Nitrogen Added	Grams Nitrogen On Resin	% Recovery
50W-X4	quinoline	.015	.012	78.
50W-X4	dimethylquinoline	.015	.0083	55.
50W-X4	aniline	.015	.0090	59.
HCRW-2	quinoline	.015	.0089	60.

city than the HCRW-2, it has a larger number of active sites per gram of resin. For equal weights of resin the 50W-X4 would have more active sites than the HCRW-2. The 50W-X4 resin would remove more of the nitrogen compounds if all the available active sites on the HCRW-2 were used and the extra sites on the 50W-X4 resin could then be used to remove extra nitrogen compounds. The cation exchange resin will have a distribution of active sites; a percentage of the sites very active for stabilization, a percentage of medium activity, and a percentage of low activity. The most effective resin will have the largest percentage of the very active sites. When these very active sites are filled, the selectivity coefficient will be less for exchange at the remaining active sites and smaller amounts of nitrogen compounds removed.

Experiments 2-2 and 2-3 investigated the effect on the separation achieved of different quantities of resin added. The experiments were done using two different resins. The results are seen in Table 3 and Table 4.

Experiment 2-3 indicates that all the nitrogen compounds could be removed using 2.6 g of Dowex HCRW-2 resin. Experiment 2-2 indicates that the removal does reach a maximum, but does not reach 100% removal. Experiment 2-3 shows a greater than 100% removal. The error reflects the

Table 3

Nitrogen Compound Removal Versus Quantity of 50W-X4 Resin

Experiment 2-2
g N added = .0296
Dowex 50W-X4 resin

g resin (dry)	g N on resin	% recovery
.7391	.0059	20.
1.3198	.011	37.
3.4117	.018	63.
5.1176	.022	74.
8.0593	.023	76.

Table 4

Nitrogen Compound Removal Versus Quantity of HCRW-2 Resin

Experiment 2-3
g N added = .0151
Dowex HCRW-2 resin

g resin (dry)	g N on resin	% recovery
.2773	0	0
1.0700	.0011	7.3
1.5779	.0079	52.
2.6350	.021	140.
5.5298	.017	110.

uncertainty associated with analysis of low absolute amounts of nitrogen present per gram of resin.

In experiments 2-4 and 2-5, the influence of acetyl chloride concentration on the separation method was studied. The results are presented in Table 5.

Two different resins were used for this experiment because the supply of HCRW-2 was depleted and additional resin could not be found. The 50W-X8 has the advantage of a larger capacity. The experiments show that the larger quantitites of acetyl chloride have a negative effect on the recovery. Only a very small amount of acetyl chloride is needed to remove the nitrogen compounds. This is supported by the molar relationship between the acetyl chloride and nitrogen. These experiments were performed with .0011 mole of nitrogen. One ml of acetyl chloride is .0140 moles. Since the reaction presumably involves one mole of nitrogen per mole of acetyl chloride, any quantity of acetyl chloride above .1 ml is a molar excess. Excess acetyl chloride may be needed in the experiments but large excesses tend to retard the reaction. This may arise from the influence of the excess acetyl chloride on the solution properties of the solvent phase. Increased solvent polarity could shift the adsorption equilibrium by decreasing the solution phase activity for the cations.

Table 5

DMQ Removal Versus Acetyl Chloride Concentration

Experiment No.	Resin	ml Acetyl Chloride	g N on Resin
2-5	50W-X8	0	.0003
2-5	50W-X8	.3	.0094
2-5	50W-X8	.8	.0092
2-5	50W-X8	1.0	.0095
2-5	50W-X8	2.0	.0091
2-4	HCRW-2	1.0	.0019
2-4	HCRW-2	2.0	.0013
2-4	HCRW-2	3.0	.0005
2-4	HCRW-2	5.0	.0007
2-4	HCRW-2	10.0	.0006

A mass balance for nitrogen was calculated from experiment 2-5. The grams of nitrogen added to each mixture was .0151 g. The mixtures were separated into decantate and resin. The weight of nitrogen in each fraction was calculated from elemental analysis (weight N = weight fraction x %N). The results are presented in Table 6. The data indicate that a mass balance can be achieved between the nitrogen added and the nitrogen on the resin and in the decantate. The difference in recovery can be attributed to the errors in nitrogen analysis.

Experiment 2-6 was a time study of the separation method. The results are in Table 7. It is seen that the maximum amount of nitrogen removal by the resin occurs within 30 minutes. This corresponds to the results from Phase 1 where the nitrogen content is reduced in 5 minutes. The extra time of these experiments may be for migration of the cation to the resin sites. In Phase I, the quantity of nitrogen reacting was determined by GC anaylsis, while in these experiments the quantity of nitrogen reacting was determined by nitrogen analysis of the resin.

Experiment 2-7 was used to determine if the separation method could remove primary and secondary amines from aromatics and saturates. Gas chromatograms from the experiment are seen in Figure 6. Figure 6 shows a chromatogram of the

Table 6

Mass Balance for DMQ Removal

(.0151 g N added to each experiment)

Experiment No.	ml Acetyl Chloride Added	g N on Resin	g N in Decantate	g N Resin + g N Decant	% Recovered
2-5	.3	.0094	.0065	.016	100.
2-5	.8	.0092	.0052	.014	95
2-5	1.0	.0095	.0045	.014	93

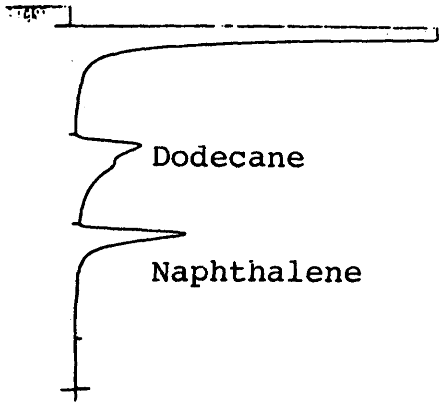
Table 7

Time Studies of DMQ Removal

Experiment Number	Time Reacted	g N Removed
2-6	5 min	.0055
2-6	15 min	.0070
2-6	30 min	.0089
2-6	60 min	.0088

Figure 6

Gas Chromatograms for Experiment 2-7



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STOP



RUN #    11

AREA%
  RT            AREA TYPE    AR/HT        AREA%
 0 44  1.8735E+07  SBB    0.134       93.657
 2.40      706990  TBV    0.567        3 534
 3.91      561890  TVP    0.266        2.809


TOTAL AREA= 2.0004E+07
MUL FACTOR= 1 0000E+00
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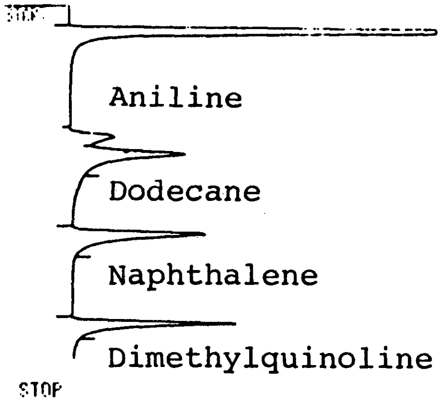

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STOP


RUN #     3

AREA%
  RT          AREA TYPE    AR/HT        AREA%
 0.39      9105000  SPB    0.090       65.772
 2 22       456210   BV    0.152        3.296
 2.51      1413300   VB    0.175       10.253
 3.89      1501400   PB    0.149       10.846
 5.42      1361300   PB    0.110        9.834


TOTAL AREA= 1.3843E+07
MUL FACTOR= 1 0000E+00
```

original mixture containing aniline, dodecane, naphthalene, and dimethylquinoline and the chromatogram of the solution from experiment 2-7 after separation from the resin. The chromatograms indicate that the aniline and dimethylquinoline were removed and the dodecane and naphthalene remained in the solution.

Phase III

These experiments were designed to investigate the utility of the separation method. Experiment 3-1 indicates that absolute alcohol will desorb a portion of the nitrogen compounds associated with the resin (See Table 8). The alcohol desorbs the nitrogen compounds by a nucleophilic displacement at the acetyl carbon producing free nitrogen compound and acetate ester plus protonated resin. Experiment 3-2 involved attempted desorption of nitrogen compounds using aqueous HCl solution. Only a small percentage of the nitrogen compounds (Table 9) was desorbed from the resin. The expected products in this approach are acetic acid, free nitrogen compound, and protonated resin. However, the excess acid may have resulted in protonation of the nitrogen compounds to form a cation associated with the resin. Sodium hydroxide solution was then mixed with the resin to deprotonate the nitrogen compounds. A substantial increase

Table 8

Desorption of Nitrogen Compounds from Resin Using Absolute Alcohol

Experiment	% N separated	% N removed from resin by alcohol
3-1	75.	22. %
3-1	78.	25. %

Table 9

Desorption of Nitrogen Compounds from Resin
Using HCl and NaOH

Experiment No.	% N separated	% N removed by HCl	% N removed by NaOH	% N removed by HCl followed by NaOH
3-2	73.	5.1	34.	37.
3-2	67.	8.1	49.	55.

in nitrogen desorption resulted (Table 9). The drying of the resin following the HCl treatment may have affected the recovery.

The nitrogen content of the synthetic crudes used in Experiment 3-3 is shown below.

Parahoe Shale Oil	2.11 % N
Utah COED Syncrude	0.478 % N
Kentucky COED Syncrude	0.226 % N

The results are seen in Table 10. Nitrogen removal was greatest for the Utah syncrude and poorest for the Parahoe Shale Oil. Dichloromethane was used as the solvent for these experiments and it might not be the best solvent for these syncrudes. It is difficult to determine the amount of nitrogen compounds solubilized by this solvent.

Table 10

Nitrogen Removal from Synthetic Crudes

Synthetic Crude Sample	g N Present	g N Removed	% N Removed
1.42 g Parahoe Shale Oil	.030	.0044	15. %
1.34 g Parahoe Shale Oil	.028	.0031	11. %
2.29 g Utah Syncrude	.011	.0030	28. %
1.00 g Utah Syncrude	.0048	.0015	31. %
3.00 g Kentucky Syncrude	.0068	.0014	21. %
3.05 g Kentucky Syncrude	.0069	.0014	21. %

CONCLUSIONS

This work has shown that nitrogen compounds can be removed from a solution phase via retention of a cation exchange resin, presumably as an acyl cation. Significant amounts of aniline and dimethylquinoline can be preferentially removed from a solution also containing naphthalene and dodecane.

Several of the different parameters that affect this reaction have been investigated; quantity of resin, quantity of acetyl chloride, and length of time for the removal to occur. It has been shown that the removal of nitrogen compounds occurs within 30 minutes, but there must be sufficient cation exchange resin present to provide active sites for all the nitrogen compounds. It has been shown that acetyl chloride is as effective in small quantities (3 mole to 1 mole nitrogen) as well as in larger quantities (20 mole to 1 mole nitrogen). A larger excess of acetyl chloride is detrimental to the separation.

The validity of the nitrogen compound removal has been supported by mass balance data. In these experiments (all run in a batch mode) the nitrogen compounds were not quantitatively removed. This could be caused by an equilibrium effect. The detrimental effect of a large excess of acetyl chloride may represent a solvent effect on the equilibrium. The separation might be improved by performing these experiments in a column mode where the acyl cations are continuously coming in contact with fresh resin.

This separation scheme was used for the separation of nitrogen compounds from synthetic crudes. The recoveries were low which could be caused by solvent effects. The model experiments were performed with a limited number of compounds present while many compounds are present in synthetic crudes. The possibility exists that the nitrogen compounds were not free to react with the acetyl chloride due to their interaction with other components. Other solvents (instead of dichloromethane) should be investigated to determine if they could improve removal by dissociating such complexes.

Attempts were made to remove the nitrogen compounds from the resin after the separation. Absolute alcohol removed small amounts but dilute HCl followed by NaOH solution did remove a greater quantity of the nitrogen compounds.

Further work must be performed to investigate the solvent effects of the acetyl chloride, to find a better solvent (instead of dichloromethane) for removal of nitrogen compounds from natural systems, and to determine the equilibrium parameters for this separation method.

Commercialization of this separation method for the removal of nitrogen compounds from synthetic crudes cannot be done until this process is developed so that it can be used in a recycle mode. The high cost of the resin would require that it be returned to its original form after desorption of the nitrogen compounds.

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