Characterization of Nitrogen-Containing Species in Coal and Petroleum-Derived Products by Ammonia Chemical Ionization - High Resolution Mass Spectrometry

Garret A. Veloski,* Ronald J. Lynn, and Richard F. Sprecher

* Author to whom correspondence should be addressed.

U.S. Department of Energy, Pittsburgh Energy Technology Center,
P.O. Box 10940, Pittsburgh, PA 15236

A coal-derived light distillate and a petroleum-derived residuum have been studied by high resolution mass spectrometry using both low-pressure ammonia chemical ionization and low-voltage electron impact ionization. A mass calibration mixture for use with ammonia chemical ionization has been developed. Selective ionization of the basic nitrogen-containing compounds by ammonia chemical ionization and compound type characterization of the resulting quasi-molecular species has been demonstrated. Several homologous series of nitrogen-containing compounds were identified in a basic extract by electron impact ionization and compared with quasi-molecular analogs identified by ammonia chemical ionization.

INTRODUCTION

The nitrogenous compounds present in coal-derived materials pose a significant challenge to process developers involved in the upgrading of fuels. Certain nitrogen-containing compounds are known to be responsible for premature catalyst deactivation in upgrading and have also been implicated as promoters of fuel instability.[1,2] Conversion of these materials to transportation fuels requires that the nitrogenous impurities be reduced to negligible levels. To determine a particular catalyst's effectiveness in heteroatom removal, it would be advantageous to compare the compound types found in the starting material and product. Efforts may then be focused on components that may be resistant to hydrotreatment or other procedures designed to effect their removal. The complexity of these product streams makes it difficult to speciate the individual compounds because of practical limitations in physical separation techniques and instrumental analysis methods.[3,4]

Low-voltage, high-resolution mass spectrometry (LVHRMS) was originally developed in order to identify the hydrocarbons contained in complex fuels.[5-7] LVHRMS analysis provides semi-quantitative ion intensity data that can be used to generate carbon number distributions for the various homologous series in many of the molecular formula classes in these materials.[3,4,8,9] However, LVHRMS is inappropriate for direct characterization of low levels of nitrogen compounds in hydrocarbon fuels because of interferences from ^{13}C contained in the abundant hydrocarbons.

The N-^{13}CH mass doublet is a common interference encountered in high resolution mass spectra. The mass difference for the N-^{13}CH doublet is 0.00815 amu, requiring a minimum baseline resolving power of approximately 1 part in 25000 at m/z 203.[10,11] Although N-^{13}CH is less difficult to resolve than some other doublets, it nonetheless becomes problematic whenever nitrogenous odd mass molecular species are one amu above a high abundance even mass molecular species. The signal arising from the organonitrogen ion is often masked by that of a ^{13}C satellite of an even mass hydrocarbon parent ion. Resolution of these ions are especially difficult because fuel analytes typically contain only small amounts of organonitrogen compounds. At lower resolutions or higher mass, the even-electron, odd mass fragment ions of hydrocarbon homologs further complicate the identification. These hydrocarbon ion fragments are frequently observed in low voltage spectra. Attempts to correct the intensities of ^{13}C ions arising from hydrocarbon molecular species have been made by attributing any intensity in excess of the statistical ^{13}C abundance to an unresolved nitrogen component, provided lower mass members of a nitrogen-containing homologous series had been identified.[3] Other approaches to dealing with this interference include HCl precipitation followed by ion exchange chromatography,[12] and trifluoroacetyl derivatization.[13]

Chemical ionization (CI) is an alternative way to produce ions while controlling selectivity and fragmentation. Ion-molecule reactions occur readily between ammonia reagent ions ($H^+(NH_3)_n$) and compounds having proton affinities exceeding 205 kcal mol^{-1}.[14] The proton affinities of most nitrogen-containing compounds range from 205-240 kcal mol^{-1}. In place of molecular species of nitrogen analytes usually observed in low voltage EI mass spectrometry, ammonia CI spectra afford primarily the protonated quasi-molecular species MH^+. Hydrocarbons do not ionize under ammonia CI conditions, therefore, N-^{13}CH interferences can be reduced in complex hydrocarbon matrices. A variation of this technique has been used successfully to characterize organonitrogen compounds in a basic fraction of a coal-derived oil using GC-MS.[15] In this GC-MS study, the base peaks in the mass spectra of the major chromatographic peaks were dominated by quasi-molecular ions of organonitrogen compounds.

In this manuscript, the advantages of ammonia chemical ionization high-resolution mass spectrometry (CIHRMS) for the detection of nitrogen compounds are demonstrated by comparing the direct analyses of a coal liquefaction product and a petroleum residuum oil by ammonia CIHRMS with analyses of extracts by LVHRMS. A simple internal calibration mixture, employing reagents that readily undergo chemical ionization under ammonia CI conditions, has been developed to aid determination of precise masses.

EXPERIMENTAL SECTION

Samples. The coal-derived liquid was obtained from Hydrocarbon Research Incorporated (HRI) and was prepared under contract for the U.S. Department of Energy. The sample consisted of a distillate cut from the naphtha stabilizer bottoms (NSB) stream taken from the proof-of-concept run #1, employing a two-stage liquefaction reactor. The petroleum-derived sample consisted of a Hondo vacuum residuum (20% 934ºF-) which was treated with hydrogen over a $NiMoS_2$ catalyst.[16] The nitrogen content of this material was 0.8%. These materials were selected because they contain organonitrogen compounds and represent the volatility range of materials typically studied by LVHRMS. The samples are not representative of all hydrotreated coal- and petroleum-derived products.

Chemical Reagents. Anhydrous ammonia 99.99% (Aldrich Chemical) was used for the chemical ionization reagent. Pyridine d_5, (99 atom % D) was obtained from MSD Isotopes. Reagents 2-fluoropyridine, 2,5-dichloropyridine, 3-bromopyridine, 2,5-dibromopyridine, 4-chloroquinoline, and 3-bromoquinoline were obtained from Aldrich Chemical and were used without further processing. A mixture of 3,5-dibromoquinoline, 3,8-dibromoquinoline and 3,5,8-tribromoquinoline was prepared using the methods of de la Mare, *et al*.[17] In addition to these compounds, an alternate synthetic approach by Denes and Chira[18] provided an isomeric mixture of bromochloro-, chlorodibromo-, chlorotribromo-, and tetrabromoquinolines. The composition of the calibration mixture for LVHRMS work is described elsewhere.[3,4,11]

Materials and Apparatus. A Kratos MS-50 double focusing high resolution mass spectrometer, equipped with a CI/EI source and interfaced to a personal computer-based data system[a], was used to acquire the high resolution CI and LVHRMS spectra. The programs used for the acquisition and subsequent data reduction were written in Microsoft® Visual C++. Acquisition hardware includes an Analogic® model HDAS-16 16 bit analog to digital converter operated in single channel acquisition mode. The sampling rate for a typical 300 sec./decade scan at 1 part in 20000 static resolution was 2kHz.

---

[a] developed at the Pittsburgh Energy Technology Center

Procedure 1: LVHRMS (EI). Samples were introduced through the direct insertion probe. The mass calibration standards and samples were delivered by the all-glass, heated-inlet system (AGHIS) maintained at 220ºC. The acceleration potential was 8kV. Ionization voltage was adjusted to provide an m/z 91/106 intensity ratio of <10% for *m*-xylene. The ion repeller was adjusted to optimize signal intensity. Resolving power was measured in the static mode at 1 part in 20000 (baseline definition) at m/z 206. The source was maintained at 200ºC and at a pressure of 5×10^{-7} torr. Details of the LVHRMS experimental protocol can be found in reference 11.

Procedure 2: CIHRMS. The source control circuitry was modified to regulate filament current based on the sum of electron emission to the electron trap and cage. This arrangement increases filament current in response to attenuation of the electron beam by the reagent gas plasma. The actual filament current was not measured. The ammonia pressure was regulated in two stages for a final reagent gas manifold pressure of 100-125mm Hg. The operating pressure during CI experiments was 5×10^{-4} torr, as measured at the source ionization gauge. The CIHRMS reference was prepared by mixing approximately equimolar quantities of pyridine d_5, 2-fluoropyridine, 2,5-dichloropyridine, 3-bromopyridine, 2,5-dibromopyridine, 4-chloroquinoline, and 3-bromoquinoline. To these were added the synthesized haloquinolines mixture (vide supra). The relative quantities of the various components in the mixture were then adjusted to provide the desired MH$^+$ intensities under ammonia CI conditions. The instrument was initially optimized for low voltage EI conditions. Approximately 0.25µl of CIHRMS calibration mixture was then introduced through the AGHIS. While observing the region surrounding the molecular ions of 3-bromoquinoline (m/z 207-210) on the oscilloscope display, the toggle valve that controls reagent gas flow to the source was opened. The intensities of the MH$^+$ molecular ions were observed to increase dramatically. This was accompanied by a simultaneous decrease in the original M$^{+\cdot}$ ion intensities. The ion repeller, electron voltage control, and ammonia pressure were then readjusted to optimize MH$^+$ and minimize M$^{+\cdot}$ in the calibration standard while maintaining the appropriate isotopic abundances. Samples were introduced using the direct insertion probe. For Hondo residuum the probe was heated to 200^{o}C. For the coal-derived NSB and related lighter material the probe was warmed by heat transfer between the ion source and contacting probe. The source was maintained at 140ºC and the static resolution was measured at 1 part in 20000 (baseline definition).

DISCUSSION OF RESULTS

Ammonia CIHRMS Mass Calibration. A fundamental problem encountered when conducting high resolution CI experiments is a lack of suitable mass calibration standards. Bowen and Field used substituted 1,3,5-triazines as markers for CH_4 and i-C_4H_{10} CI.[19] Bertrand *et al*. found a mixture of polydimethylsiloxanes (PMS) suitable for high resolution CI using CH_4 and i-C_4H_{10} as reagent gases.[20] Few ammonia CIHRMS calibration schemes have been reported in the literature. The usual mass standards such as perfluorokerosene (PFK), perfluorotri-*n*-butylamine (PFTBA) , and polyfluoropropylene oxide (Fomblin-18/8) were reported to be unsatisfactory under ammonia CI conditions.[20-22] PMS were reported to be only marginally useful for ammonia CI.[20] Brinded and coworkers tested the nonionic detergent Triton-x 100 and similar preparations as an ammonia CIHRMS reference.[21] The mixture generated primarily $M\text{-}NH_4^+$ adduct ions for each oligomer providing a calibration range of $268 < m/z < 1105$. Pergantis *et al*. employed a mixture of ammonia and methane to obtain accurate mass measurements on pure compounds.[22] Reportedly, the mixed reagent gas produced the familiar PFK reference masses and sufficient ion intensity was achieved for calibration purposes.

As a starting point in this investigation, PMS and Triton-x 100 were also tested as mass calibration standards for ammonia CIHRMS. The mixed gas approach of Pergantis, *et al*. was not pursued. Mass measurements and relative abundances for the principle ion series of PMS were successfully obtained under EI conditions. However, under ammonia CI conditions, the observed ion abundances were too low to be useful for calibration purposes. The ammonia CI spectrum of Triton-x 100 appeared unduly complex and yet was at the same time, conspicuously devoid of suitable reference ions below about m/z 268. A significant portion of analyte ion intensity may be below m/z 268, especially for certain distillates. Additionally, the reported reference ions in Triton-x 100 were not mass deficient and could interfere with certain analyte masses.

The calibration mixture used in LVHRMS consists of halogenated 1- and 2-ring aromatic hydrocarbons.[7] The mixture was formulated to provide adequately spaced, abundant, mass deficient molecular ions at low ionizing voltages. These characteristics are very important for mass calibration software that depends heavily on the user's ability to recognize reference ions. Our ammonia CIHRMS calibration mixture was designed with these attributes in mind. It consists of a simple mixture of compounds that readily undergo chemical ionization with ammonia. Although monoisotopic elements such as fluorine are desirable, identification of the reference ions is simplified by the characteristic isotope splitting patterns from compounds containing elements such as bromine and chlorine. All reference compounds afford primarily MH^+ under the conditions used (Table I). The $M\text{-}NH_4^+$ adduct ion was sufficiently abundant to serve as an additional reference in some instances. Components of the ammonia CI reference mixture can be added or deleted to meet the needs of the experiment. As can be seen in Table I, most of the primary reference ions and ammonium adduct ions, are mass deficient. For comparison, defects for quasi-molecular mononitrogen analytes ($[C_nH_{2n\text{-}Z}N]H^+$) range from about 0.0500-0.4570 between m/z 68 and m/z 408. Although the fractional mass of pyridine-d_5 is in the range of some analytes, it occurs at odd mass, and does not interfere with any quasi-molecular analyte ions arising from the analysis of compounds containing an odd number of nitrogen atoms. The mass range is adequate for volatile components typically analyzed in fuel mixtures. The reference mixture and ion masses in Table I were used for calibration of the ammonia CIHRMS data presented.

Selection of Elemental Composition Data.

Each measured mass in the calibration range was first processed by calculating a set of elemental compositions using a combinatorial analysis algorithm. The best elemental compositions were then selected from these sets based upon specific criteria. For LVHRMS data, elemental compositions for the isotopically most abundant molecular ions must obey the nitrogen rule, i.e., combinations with odd numbers of nitrogen atoms must occur at odd mass to be considered as a molecular specie. Constraints were then used to place practical limits on hydrogen deficiency (Z number) as well as the total number of the heteroatoms (N,O, and S) used in the calculation of ion compositions. When these criteria have been satisfied, the deciding factor becomes the difference between the calculated mass of the candidate elemental composition and the measured mass. Selection of elemental compositions for quasi-molecular ion species obtained by ammonia CI is similar in all aspects except the nitrogen rule. Combinations with odd numbers of nitrogen must occur at even mass to be considered. The abundances of the $M^{+\cdot}$ and MH^+ ion species are expressed as a percentage of the total sample ion intensity and are not corrected for relative ionization efficiency or isotopic contributions. Reference masses and their satellites were excluded from the final report.

Analysis of Complex Mixtures

Both LVHRMS and ammonia CIHRMS were used to identify the nitrogen-containing compound types in a coal-derived naphtha stabilizer bottoms (NSB), a basic extract prepared from the NSB, and a hydrotreated Hondo crude vacuum residuum oil. Table II compares carbon number distributions for the mononitrogen formula classes and 12 structural types determined by LVHRMS ($C_nH_{(2n-Z)}$ N) and ammonia CIHRMS ($[C_nH_{(2n-Z)}N]H^+$) for NSB basic extract and whole NSB. There were 82 individual molecular ion homologs found by LVHRMS in the basic fraction of NSB. The majority of the ion intensity was distributed among the homologous series Z=5 to Z=13 and dominated by Z=5 which are most likely a mixture of alkylpyridines and alkylanilines. Ammonia CIHRMS of the same sample found 60 quasi-molecular homologs belonging to the class $[C_nH_{(2n-Z)}N]H^+$. Likewise, the majority of ion intensity was in Z=5 to Z=13 structural types. Additionally, a series of quasi-molecular ion homologs was observed at Z= -1. The elemental compositions for members in this series are consistent with protonated cycloalkylamines. The molecular ions of cycloalkylamines are very susceptible to radical site initiated ion decomposition (alpha cleavage) giving rise to abundant even-massed nitrogen-containing homologous ion series. These ions would be excluded from the LVHRMS report because they are not valid molecular species. Unexpectedly, the ammonia CIHRMS data for whole NSB product contained 95 homologous species. The additional homologous members reside mainly in the Z=1 and Z=3 series. These compounds could have been lost to evaporation during the preparation of the basic extract.

The histograms presented in Figures 1 and 2 show a similar distribution of both molecular and quasi-molecular species determined by LVHRMS and ammonia CIHRMS data acquired on the basic extract. Although it was not confirmed, the ammonia CI data most likely consists of protonated analogs of the molecular ions detected by LVHRMS. Many of these same $[C_nH_{(2n-Z)}N]H^+$ quasi-molecular species found in the basic extract can also be observed in Figure 3 which graphically represents the results of the ammonia CIHRMS experiment conducted on whole NSB. Except for the lower molecular weight members, the homologous series of quasi-molecular ions in Figure 3 are remarkably similar to those of the extract (Figure 2) despite the relatively low (115ppm) nitrogen content and complexity of the mixture. No organonitrogen compositions could be identified with certainty by LVHRMS in whole NSB. This was not surprising, considering the overwhelming interference of the hydrocarbon ^{13}C species and low nitrogen content.

The greatest difference between the EI and CI data can be readily observed in the relative intensity profiles for homologous members of the Z=5 and Z=7 series found in the basic extract. In the basic extract, the Z=5 and Z=7 compound types most likely consist of alkylpyridines and alkyltetrahydroquinolines, respectively. Alkyltetrahydroquinolines and other hydroaromatics, can undergo partial dehydrogenation in the all-glass, heated-inlet system. That portion of the alkyltetrahydroquinolines that do survive the heated inlet are then susceptible to fragmentation even at low ionizing voltages. NIST library EI spectra[23] of various isomers of alkyltetrahydroquinolines, alkyltetrahydroisoquinolines, as well as some non-pyridinic isomers such as alkyl-2,3-dihydro-1H-indoles, all exhibit high abundance even mass fragment ions. EI sensitivities for hydroaromatics vary inversely with the degree of corresponding aromatic ring saturation.[3] Unless compensated through the application of experimentally obtained sensitivity correction factors, these phenomena result in ion intensities that do not reflect the actual concentrations in the mixture. In terms of coal liquefaction chemistry, accurate monitoring of the aromatic/hydroaromatic ratio among nitrogen-containing species as a result of changing experimental parameters is helpful in developing a strategy for their removal.

The organonitrogen types in Hondo petroleum residuum were also characterized by ammonia CIHRMS. The ammonia CIHRMS spectrum is provided in Figure 4. The elemental compositions derived for most major peaks occurring at even mass in Figure 4 contain a nitrogen atom. The numbered peaks are members of the most abundant homologous series of ions (Z=17) which also contains the base peak ($[C_{20}H_{23}N]H^+$). The precise mass data presented in Table III compares the measured masses for the Z=17 homologous series members with the theoretical masses calculated from the selected quasi-molecular ion elemental compositions. The average absolute deviation from the calculated masses for these 17 members was about 7.1ppm

Almost 1300 analyte ions were identified for Hondo residuum within the calibrated mass range. A significant number of these ions and ion fragments had elemental compositions consistent with both odd and even mass hydrocarbons. Over 300 of these ion species had elemental compositions consistent with quasi-molecular nitrogen species. Carbon number distributions for 217 identified quasi-molecular homologs belonging to the formula class $[C_nH_{(2n-Z)}N]H^+$ are sorted into 16 classes and presented in Table IV. Over 95% of the total analyte ion intensity was contributed by the 16 distinct structural types in this class which consisted primarily of 3 and 4 ring azaarene or aromatic amine compounds. Each molecular formula within a specific Z series represent many possible structural and position isomers (alkylated members). An additional 96 homologs containing 1 nitrogen atom and 1 oxygen atom were found. These comprised about 4.5% of the analyte intensity. Schmidt and coworkers identified a $C_nH_{(2n-Z)}NO$ class of compounds by LVHRMS in the basic subfraction of a dialyzed coal liquid[3], and a pyridine dialyzate of an Illinois No. 6 coal.[10] These were found to be amphoteric in nature.

The high selectivity of ammonia CI did not totally eliminate interferences. Frequently, ion species having both even and odd mass hydrocarbon compositions ($C_nH_{(2n-Z)}$ and $C_nH_{((2n-1)-Z)}$) were observed in the ammonia CI spectra of both Hondo residuum and NSB products. Although NH_4^+ does not protonate hydrocarbons, that is not to say that hydrocarbon ion species cannot arise through charge transfer with $NH_3^{+\cdot}$ also present during CI experiments, or by the action of free electrons in the source. $M^{+\cdot}$ ions are frequently observed in ammonia CI spectra.[24] The higher electron potentials used for CI would also be capable of inducing fragmentation of hydrocarbons in the sample. Odd mass molecular ions of mononitrogen species ($C_nH_{(2n-Z)}N^{+\cdot}$) were also evident in the spectra. These ions accounted for only a small portion of the total intensity and were not reported.

Interestingly, a number of ammonia CI induced isobaric interferences can occur. As illustrated in Figure 5, the ammonia adduct ion ($[MH(NH_3)]^+$) of a compound such as diphenylamine will have the same elemental composition as the MH^+ ion arising from the dinitrogen compound tetramethylquinoxaline.

Dinitrogen species were discovered to arise from a number of compounds used in the CI reference mixture. For the haloquinolines we believe these ions are the result of substitution reactions of the type

$$[C_9H_6NX]^{+\cdot} + NH_3 \longrightarrow [C_9H_6N]NH_3^+ + X^\cdot$$

between haloquinoline molecular ions and ammonia. Similar reactions are known to occur with substituted benzenes.[24] Ammonia substitution product ions arising from the monohalogenated ammonia CI reference compounds provide elemental compositions that are also indistinguishable from protonated dinitrogen analytes. No dinitrogen compositions in addition to those previously identified in the reference mixture were found in either Hondo residuum or the coal-derived NSB. Equally troublesome are the ammonia CI spectra of certain polyfunctional aromatic ethers and phenols which have reportedly given rise to ion species of the type $[M+H-H_2O]^+$ and $[M+NH_4-H_2O]^+$, the latter of which would be indistinguishable from quasi-molecular ions arising from a mononitrogen compound.[25,26]

Figure 6 displays an example of an actual N-CH_2 doublet encountered in the ammonia CIHRMS spectrum of untreated NSB. The static resolution measured at the beginning of the scan was 1 part in 20000 at m/z 206 (MH^+ of 3-bromoquinoline). The mass difference between m/z 206.2042 and m/z 206.1918 is ~ 0.0124amu. At a resolution of 1 part in 20000 this doublet should be baseline resolved. The analog data in figure 6 suggests otherwise. An explanation can be offered based on the presence of an unresolved component. Indeed, there is a peak at m/z 205.1956 having the composition $C_{15}H_{25}$. The statistical ^{13}C intensity of m/z 205.1956 would place the unseen component ($^{13}CC_{14}H_{25}$) directly below the valley at m/z 206.1990. Fortunately, the N-CH_2 mass difference of 0.0126 amu is substantially larger than 0.00815 amu for N-^{13}CH doublet. In addition, the ^{13}C species arising from the odd mass hydrocarbon ions were generally of low relative abundance, and therefore, do not interfere with any but the lowest intensity even mass quasi-molecular nitrogen species. Overall, much less interference is encountered in the characterization of organonitrogen compounds in complex hydrocarbon matrices by ammonia CIHRMS than by the LVHRMS technique. This alone is a significant improvement.

SUMMARY

The reference mixture presented herein provides abundant, easily identified, and adequately spaced precise mass markers for the calibration of high resolution ammonia CI mass data for use with single-beam, double-focusing instruments.

The combination of ammonia CI selectivity and high precision mass measurement expands the capabilities of batch mode analysis of complex mixtures and represents a considerable advantage over LVHRMS for determination of low abundance organonitrogen analytes. CIHRMS data can also assist in the process of interpreting elemental composition assignments made by LVHRMS in instances where there is the possibility of strong N-^{13}CH interference.

LITERATURE CITED

(1) Fathoni, A. Z.; Batts, B. D. *Energy & Fuels* **1992**, *6*, 681-693.

(2) White, C.M.; Schweighardt, F.K.; Schultz, J.L. *Fuel Processing Technology*, 1078, 1, 209-215.

(3) Batts, B.D. In <u>Spectroscopic Analysis of Coal Liquids</u>, Kershaw, J.R. eds., Elsevier, New York, NY, pp. 61-128, (1989).

(4) White, C. M. In <u>Polycyclic Aromatic Hydrocarbons</u>, Bjørseth, A., eds., Marcel Dekker: New York, NY, pp. 525-616, (1983).

(5) Lumpkin, H. E. *Anal. Chem*. **1964**, *36*, 2399-2401.

(6) Johnson, B. H.; Aczel, T. *Anal. Chem*. **1967**, *39*, 682-685.

(7) Aczel, T.; Allan, D. E.; Harding, J. H; Knipp, E. A. *Anal. Chem*. **1970**, *42*, 341-347.

(8) Schweighardt, F.K.; White, C.M.; Friedman, S.; Schultz, J.L. ACS Division of Fuel Chem. 22, no. 5, 124-134.

(9) Ciocco, M.V.; Cugini, A.V.; Rothenberger, K.S.; Veloski, G.A.; Schroeder, K.T. "Effect of Pressure of First Stage Coal Liquefaction with Dispersed Catalysts", *Proceedings of the Eleventh Annual International Pittsburgh Coal Conference*, Pittsburgh, PA, pp. 500-505, (1994).

(10) Schmidt, C.E.; Sprecher, R. F. In Novel Techniques in Fossil Fuel Mass Spectrometry, ASTM STP, 1019, Ashe, T.R. and Wood, K. V., eds., American Society for Testing and Materials: Philadelphia, PA, pp. 116-132, (1989).

(11) Schmidt, C.E.; Sprecher, R. F.; Batts, B.D. *Anal. Chem.* **1987**, *59*, 2027-2033.

(12) Finseth, D.H.; Przybylski, Z.T.; Schmidt, C.E. *Fuel* **1982**, *61*, 1174-1176.

(13) Wood, K.V.; Schmidt, C.E.; Cooks, R.G.; Batts, B.D. *Anal. Chem.* **1984**, *56*, 1335-1338.

(14) Harrison, A. G. In Chemical Ionization Mass Spectrometry; CRC: Boca Raton, FL, Chapt. 4, (1983).

(15) Buchanan, M. V. *Anal. Chem.* **1982**, *54*, 570-574.

(16) Bockrath, B.C.; Parfitt, D.S. In Coal Science, *Proceedings from the Eighth International Conference on Coal Science*, Pajares, J.A. and Tascon, J.M.D. eds., Elsevier: NY, New York, pp. 1343-1346, (1995).

(17) de la Mare, P.B.D.; Kiamud-din, M.; Ridd, J.H. *J. Chem. Soc.* **1960**, 561-565.

(18) Denes, V.; Chira, R. *J. prakt. Chem.* **1991**, *320*, 351-353.

(19) Bowen, D. E. V.; Field, F. H. *Anal. Chem.* **1975**, *47*, 2289-2292.

(20) Bertrand, M. J.; Maltais, L.; Evans, M.J. *Anal. Chem.* **1987**, *59*, 194-197.

(21) Brinded, K. A.; Tiller, P. A.; Lane, S. J. *Rapid Commun. in Mass Spec.* **1993**, *7*, No. 11. 1059-1061.

(22) Pergantis, S.A.; Emond, C.A.; Madilao, L.L.; Eigendorf, G.K. *Org. Mass Spectrometry*, **1994**, *29*, 439-444.

(23) Stein, S.E.; Mallard, W.G., “NIST/EPA/NIH Mass Spectral Library”, version 1.1a, National Institute of Standards and Technology, Gaithersburg, MD, (1995).

(24) Westmore, J.B.; Alauddin, M.M. *Mass Spectrometry Reviews* **1986**, *5*, 381-465.

(25) Keough, T.; DeStefano, A.J. *Org. Mass Spectrometry* **1981**, *16*, 527-533.

(26) van der Hage, E.R.; Weeding, T.L.; Boon, J.J. *Journal of Mass Spectrometry* **1995**, *30*, 541-548.

DISCLAIMER

Table I. Reference ion masses used for the calibration of ammonia chemical ionization, high-resolution mass spectrometry (CIHRMS) data.

Reference Compound	Composition of Reference Ion	Calculated Mass of Reference Ion
pyridine-d_5	$[C_5D_5N]H^+$	85.0809
2-fluoropyridine	$[C_5H_4NF]H^+$	98.0406
†2-fluoropyridine	$[C_5H_4NF]NH_4^+$	115.0672
2,6-dichloropyridine	$[C_5H_3N^{35}Cl_2]H^+$	147.9721
3-bromopyridine	$[C_5H_4N^{79}Br]H^+$	156.9527
4-chloroquinoline	$[C_9H_6{}^{35}ClN]H^+$	164.0267
†3-bromopyridine	$[C_5H_4N^{79}Br]NH_4^+$	174.9871
2,3,5-trichloropyridine	$[C_5H_2N^{35}Cl_3]H^+$	181.9331
3-bromoquinoline	$[C_9H_6N^{79}Br]H^+$	207.9762
†3-bromoquinoline	$[C_9H_6N^{79}Br]NH_4^+$	225.0027
2,5-dibromopyridine	$[C_5H_4N^{79}Br^{81}Br]H^+$	237.8690
‡bromochloroquinolines	$[C_9H_4N^{35}Cl^{79}Br]H^+$	240.9294
†2,5-dibromopyridine	$[C_5H_4N^{79}Br^{81}Br]NH_4^+$	254.8956
3,5-dibromoquinoline	$[C_9H_5N^{79}Br^{81}Br]H^+$	287.8847
†3,5-dibromoquinoline	$[C_9H_5N^{79}Br^{81}Br]NH_4^+$	304.9112
3,5,8-tribromoquinoline	$[C_9H_4N^{79}Br_2{}^{81}Br]H^+$	365.7952
†3,5,8-tribromoquinoline	$[C_9H_4N^{79}Br_2{}^{81}Br]NH_4^+$	382.8217
‡chlorotribromoquinolines	$[C_9H_3N^{35}Cl^{79}Br_3]H^+$	397.7582
‡tetrabromoquinolines	$[C_9H_3N^{79}Br_2{}^{81}Br_2]H^+$	445.7036

† M-NH_4^+ adduct ion

‡ isomeric purity undetermined

Table II. Carbon number distributions for naphtha stabilizer bottoms (NSB) and NSB basic extract determined by low-voltage, high-resolution mass spectrometry (LVHRMS) and ammonia chemical ionization, high-resolution mass spectrometry (CIHRMS).

	Carbon Number Range			Percentage of $[C_nH_{(2n-z)}N]^+$ or $[C_nH_{(2n-z)}N]H^+$ Ion Class Intensity		
Product:	NSB basic extract		NSB (whole)	NSB basic extract		NSB (whole)
Z number	LVHRMS	NH_3 CIHRMS	NH_3 CIHRMS	LVHRMS	NH_3 CIHRMS	NH_3 CIHRMS
-1	none	C_{11}-C_{15}	C_5-C_{16}	none	0.40	2.93
1	C_6-C_{13}	C_{11}-C_{15}	C_5-C_{17}	0.15	0.96	6.37
3	C_4-C_{15}	C_{10}-C_{16}	C_5-C_{17}	0.78	1.65	4.35
5	C_6-C_{15}	C_9-C_{16}	C_5-C_{17}	49.66	17.61	15.85
7	C_8-C_{16}	C_9-C_{17}	C_7-C_{17}	29.27	49.66	35.77
9	C_8-C_{17}	C_9-C_{17}	C_8-C_{16}	7.63	15.87	15.65
11	C_9-C_{18}	C_9-C_{17}	C_{10}-C_{17}	8.50	10.14	13.03
13	C_{10}-C_{17}	C_{11}-C_{16}	C_{11}-C_{17}	2.76	3.48	4.52
15	C_{12}-C_{18}	C_{14}-C_{15}	C_{12}-C_{18}	0.61	0.13	1.28
17	C_{11}-C_{16}	C_{14}	C_{16}-C_{17}	0.32	0.11	0.19
19	C_{11}-C_{17}	none	C_{18}	0.30	none	0.06
21	C_{15}	none	none	0.02	none	none

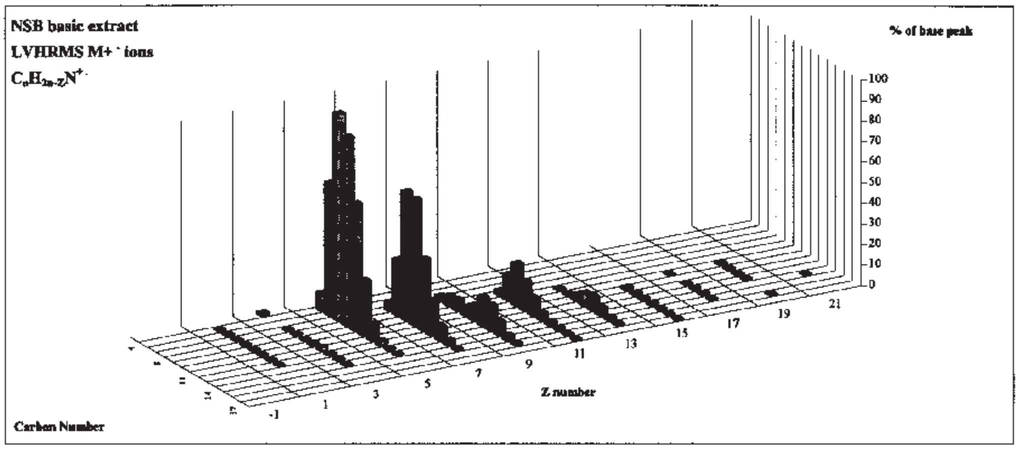


Figure 1. Mononitrogen molecular ion homologs in a basic extract from a coal-derived naphtha stabilizer bottoms fraction detected by low-voltage, high-resolution mass spectrometry.

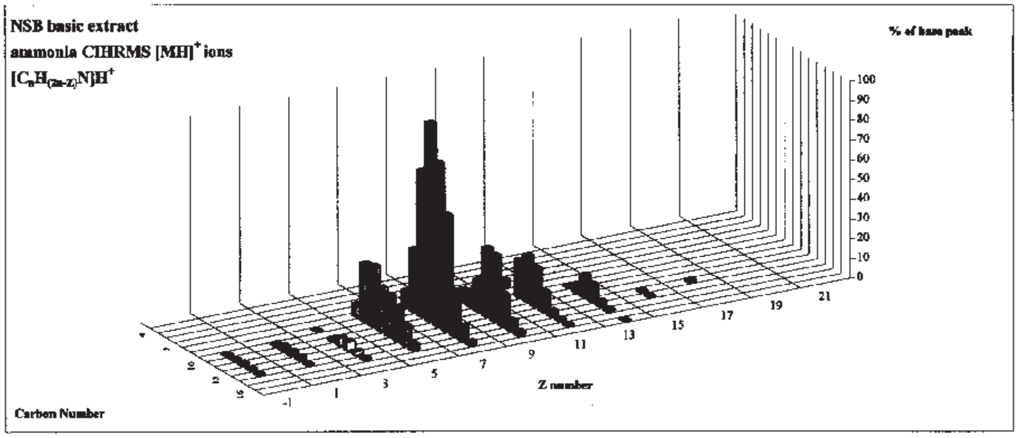


Figure 2. Mononitrogen quasi-molecular ion homologs in a basic extract from a coal-derived naphtha stabilizer bottoms fraction detected by ammonia chemical ionization, high-resolution mass spectrometry.

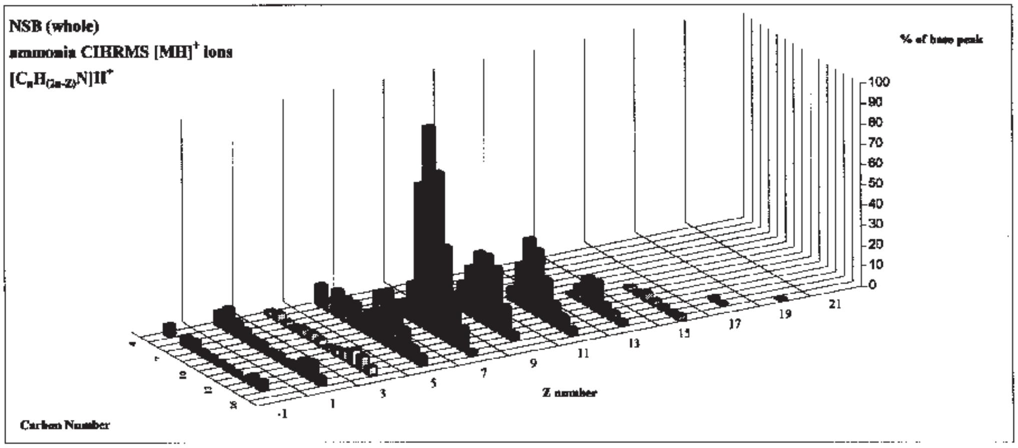


Figure 3. Mononitrogen quasi-molecular ion homologs in a whole coal-derived naphtha stabilizer bottoms fraction detected by ammonia chemical ionization, high-resolution mass spectrometry.

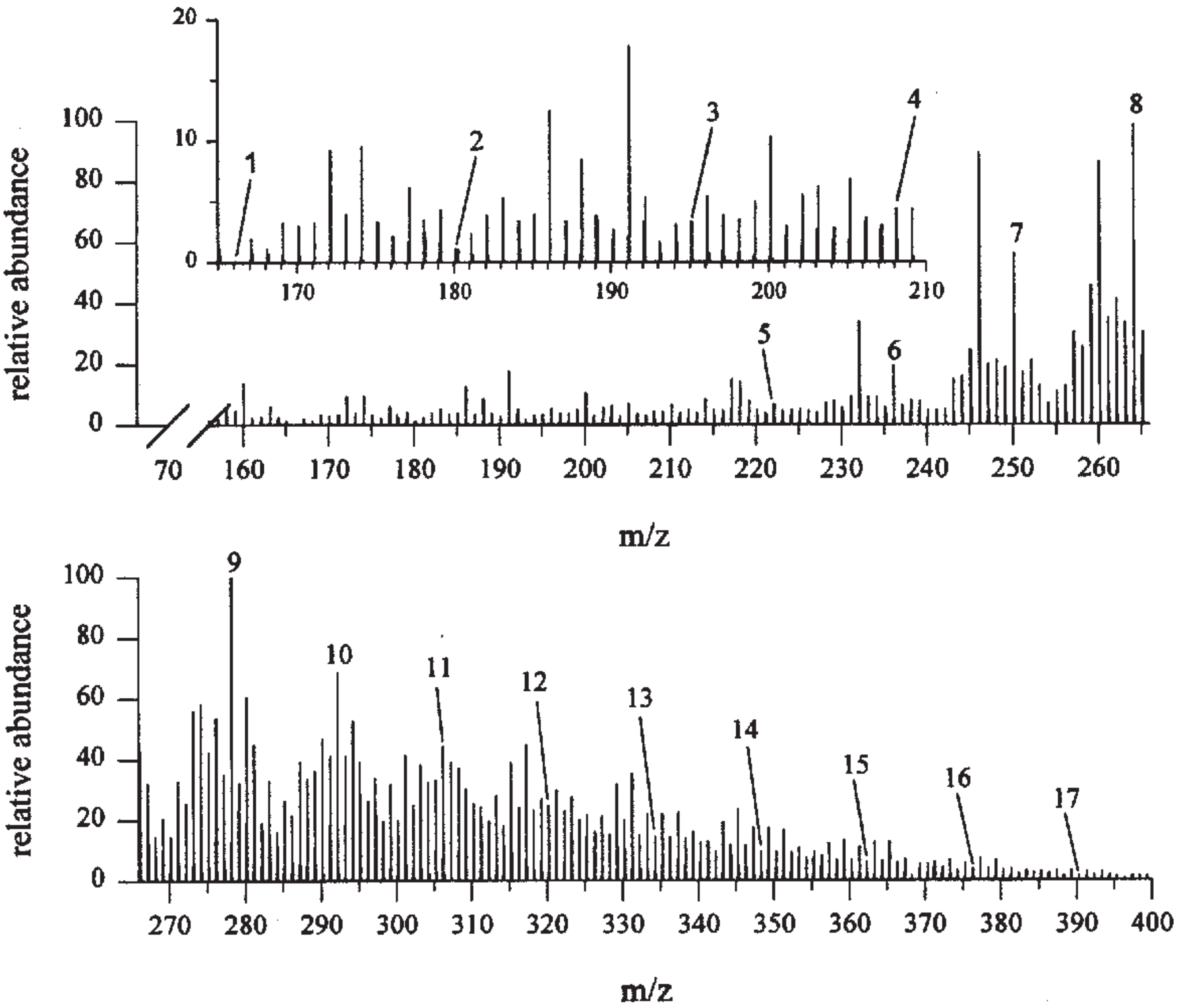


Figure 4. Ammonia CIHRMS spectrum of Hondo crude residuum. The numbered peaks indicate members of the most abundant series of homologous quasi-molecular ions (Table 3).

Peak #	Measured Mass	Calculated Mass	% of Base Peak	Elemental Composition
1	166.0686	166.06570	0.1	$C_{12}H_8N$
2	180.0822	180.08135	1.1	$C_{13}H_{10}N$
3	194.0978	194.09700	3.1	$C_{14}H_{12}N$
4	208.1148	208.11265	4.4	$C_{15}H_{14}N$
5	222.1304	222.12830	6.6	$C_{16}H_{16}N$
6	236.1434	236.14395	19.2	$C_{17}H_{18}N$
7	250.1591	250.15960	56.2	$C_{18}H_{20}N$
8	264.1754	264.17525	98.6	$C_{19}H_{22}N$
9	278.1920	278.19090	100.0	$C_{20}H_{24}N$
10	292.2081	292.20655	68.7	$C_{21}H_{26}N$
11	306.2217	306.22220	44.3	$C_{22}H_{28}N$
12	320.2402	320.23785	24.5	$C_{23}H_{30}N$
13	334.2575	334.25350	14.6	$C_{24}H_{32}N$
14	348.2732	348.26915	9.4	$C_{25}H_{34}N$
15	362.2891	362.28480	6.1	$C_{26}H_{36}N$
16	376.3052	376.30045	3.8	$C_{27}H_{38}N$
17	390.3177	390.31610	1.7	$C_{28}H_{40}N$

Table III. Precise masses and elemental compositions determined by ammonia CIHRMS for the homologous members of the most abundant quasi-molecular ion series detected in Hondo crude residuum. The numbered peaks appear in Figure 4.

Z number	% $[C_nH_{(2n-z)}N]H^+$ Formula Class Ion Intensity	% Total Sample Ion Intensity	Representative Compound Types including alkyl derivatives
-1	0.67	0.64	cycloalkylamines
1	0.77	0.73	z=1
3	0.97	0.92	pyrroles
5	2.69	2.57	pyridines, anilines
7	2.21	2.11	azaindans, tetrahydroquinolines
9	6.23	5.95	dihydroquinolines, indoles
11	7.89	7.53	quinolines
13	7.29	6.96	phenylpyridines
15	13.52	12.91	carbazoles, azafluorenes
17	20.64	19.70	acridines, phenylindoles
19	12.39	11.83	benzo[def]carbazoles, benzo[ghi]azafluorenes
21	14.88	14.21	azapyrenes, benzocarbazoles
23	5.99	5.72	benzacridines, phenylcarbazoles
25	2.18	2.08	benzo[ghi]azafluoranthenes
27	0.65	0.62	benzazapyrenes, dibenzocarbazoles
29	1.04	0.99	dibenzacridines, naphthylcarbazoles

Table IV. Ion intensity summary for $[C_nH_{(2n-z)}N]H^+$ quasi-molecular ion species identified in Hondo crude residuum**.**

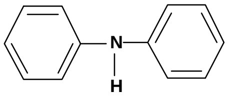
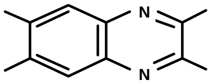
Compound	$M^{+\cdot}$	MH^+	$M\text{-}NH_4^+$
diphenylamine 	$C_{12}H_{11}N$	$C_{12}H_{12}N$	**$C_{12}H_{15}N_2$** m/z 187.1235
2,3,6,7-tetramethylquinoxaline 	$C_{12}H_{14}N_2$	**$C_{12}H_{15}N_2$** m/z 187.1235	$C_{12}H_{18}N_3$

Figure 5. Example of ammonia CIHRMS isobaric interference. The ammonia adduct ion M-NH$_4^+$ from diphenylamine has exactly the same mass and elemental composition as MH$^+$ from 2,3,6,7-tetramethylquinoxaline.

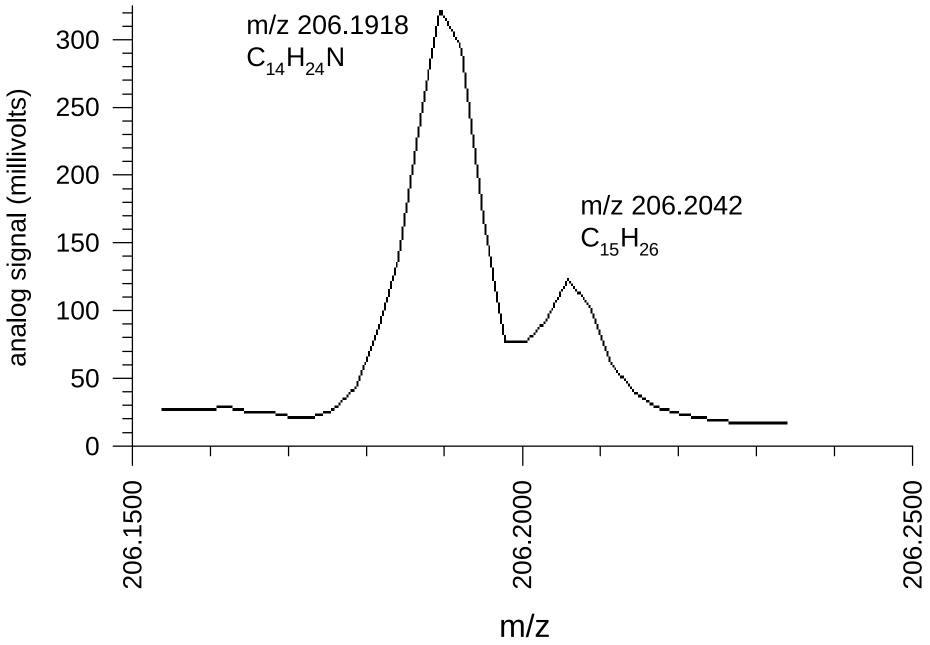


Figure 6. Plot of analog signal data of m/z 206 N-CH_2 doublet in ammonia CIHRMS spectrum of whole NSB.