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RAPID ESTIMATION OF ORGANIC NITROGEN IN OIL SHALE WASTEWATERS

B.M. Jones, G.J. Harris, and C.G. Daughton

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ABSTRACT

Many of the characteristics of oil shale process wastewaters (e.g., malodors, color, and resistance to biotreatment) are imparted by numerous nitrogenous heterocycles and aromatic amines. For the frequent performance assessment of waste treatment processes designed to remove these nitrogenous organic compounds, a rapid and colligative measurement of organic nitrogen is essential.

Quantification of organic nitrogen in biological and agricultural samples is usually accomplished using the time-consuming, wet-chemical Kjeldahl method. For oil shale wastewaters, whose primary inorganic nitrogen constituent is ammonia, organic Kjeldahl nitrogen (OKN) is determined by first eliminating the endogenous ammonia by distillation and then digesting the sample in boiling H_2SO_4. The organic material is oxidized, and most forms of organically bound nitrogen are released as ammonium ion. After the addition of base, the ammonia is separated from the digestate by distillation and quantified by acidimetric titrimetry or colorimetry. The major failings of this method are the loss of volatile species such as aliphatic amines (during predistillation) and the inability to completely recover nitrogen from many nitrogenous heterocycles (during digestion).

Within the last decade, a new approach has been developed for the quantification of <u>total</u> nitrogen (TN). The sample is first combusted, and the nitrogen is quantified by chemiluminescence. Aqueous samples containing organic and inorganic nitrogen species are combusted in an oxygen atmosphere at 1100°C to produce nitric oxide (NO) which is reacted with ozone to yield electronically excited nitrogen dioxide (NO_2^*). The light quanta emitted during relaxation of the metastable NO_2^* are quantified by a photomultiplier. Each determination requires 90 seconds.

In contrast to the utility of combustion/chemiluminescence (C/CL) for total nitrogen analysis, a rapid and reliable method does not exist for quantifying <u>organic</u> nitrogen directly. Organic nitrogen can only be determined indirectly by subtracting ammoniac-N values (determined by a separate method) from C/CL-TN values; this approach, however, compounds the errors of two methods. We have obviated this problem by developing a method for the direct determination of organic nitrogen that uses a rapid reverse-phase fractionation method for separating nonpolar from polar nitrogen in oil shale wastewaters. An aqueous sample is applied to an activated C_{18} reverse-phase cartridge. The majority of the inorganic nitrogen (primarily ammonia) and polar nitrogen compounds remain with the aqueous effluent, whereas nonpolar organic nitrogen is retained. The retained solutes are eluted with methanol. The methanolic eluate (lipophilic fraction; LpF) is analyzed for total nitrogen using C/CL. Total LpF-nitrogen (LpF-TN) values obtained for nine oil shale wastewaters proved to be a consistent underestimator of OKN. From 8% to 24% of the organic nitrogen was sufficiently polar to be collected with the ammonia in the hydrophilic fraction and the nonpolar nitrogen recovered by LpF-TN was generally from 48% to 100% of the OKN. Although the LpF-N was not equivalent to OKN, this new method may be the simplest means available for obtaining a direct, rapid <u>estimate</u> of organic nitrogen in oil shale process waters.

INTRODUCTION

The heterogeneous organic polymers that compose oil shale kerogen can be thermally decomposed into petroleum-like crude oil by pyrolytic retorting processes. In addition to oil, retorting also generates a large stream of wastewater that extracts many of the nitrogenous organic compounds from the cogenerated shale oil. The majority of the dark amber/brown color and noxious odor associated with these process waters can be attributed to nitrogenous heterocycles and aromatic amines, which account for a large portion of the organic nitrogen; many of these compounds have mutagenic potential (Santodonato and Howard 1981). Furthermore, the resistance of these

classes of nitrogen compounds to microbial degradation has been postulated to account for the failure of biological treatment schemes to upgrade these waters (Jones et al. 1981). Of the organic carbon that resists biodegradation, subsequent research has shown that most of it is associated with nitrogen (Healy et al. 1983; Torpy, Luthy, and Raphaelian 1982).

The importance of organic nitrogen in aqueous synfuel effluents has been underscored by the U.S. Environmental Protection Agency. To establish a data base and for baseline monitoring, it has been recommended that nitrogenous organic compounds be monitored in any stream unique to a particular synthetic fuel industry (Henschel and Stemmle 1983), even though these compounds are not currently priority pollutants. Although individual compounds can be determined by gas-liquid chromatography with nitrogen-specific detection, a rapid and colligative measurement for total nitrogen would be preferred for the frequent assessment of waste treatment processes designed to remove nitrogenous organic compounds from aqueous waste streams.

BACKGROUND

The undiscerning application of an unvalidated analytical method to a complex waste stream, such as oil shale process water, may yield uninterpretable data. For example, it has been reported that the organic Kjeldahl nitrogen (OKN) concentration of an ammonia-stripped, ozonated oil shale retort water (Oxy-6) exceeds the OKN of the raw water (Torpy et al. 1982). This could occur only if the oxidative treatment altered refractory nitrogenous organic compounds so that the nitrogen became susceptible to Kjeldahl digestion. To validate a method for use with oil shale wastewaters, the recovery of nitrogen from representative members of the major classes of nitrogenous compounds present in these wastewaters, the assurance of the absence of matrix effects, and the precision of recovery must be investigated.

Kjeldahl Analysis

The quantification of total and organic nitrogen in solid and aqueous samples has been traditionally accomplished using the time-consuming, wet-chemical Kjeldahl method. Total Kjeldahl nitrogen (TKN) is determined by digesting a sample in boiling sulfuric acid in the presence of a metal catalyst (e.g., mercury, copper, or selenium). During the digestion, intramolecular water is first removed from the organic compounds. Trinegative nitrogen is then released as ammonium ion, and carbon is oxidized to carbon dioxide by sulfuric acid, which is reduced to sulfur dioxide. The sulfur dioxide is then available to reduce a portion of the more oxidized forms of nitrogen to ammonia (Bradstreet 1965). The ammonia is separated from the digestate by distillation and quantified by acidimetric titrimetry or colorimetry. The procedure for organic Kjeldahl nitrogen (OKN) is identical to the TKN method except that endogenous free ammonia is eliminated by distillation prior to sample digestion.

Since the Kjeldahl method was developed specifically for proteinaceous nitrogen, it is directly applicable only to determining organic nitrogen in biological and agricultural samples. Its applicability to samples of nonbiological origin has major failings, including the loss of volatile compounds such as aliphatic amines (during predistillation) and the incomplete recovery of nitrogen (during digestion) from many nitrogenous heterocycles and from highly oxidized nitrogen species.

Combustion/Chemiluminescence

During the last decade, a new approach has been developed for the quantification of total nitrogen based on combustion followed by chemiluminescent detection (C/CL). Aqueous samples containing organic and inorganic nitrogen species are combusted in an oxygen atmosphere at 1100°C to produce nitric oxide (NO) which is reacted with ozone to yield either nitrogen dioxide (NO_2) or electronically excited nitrogen dioxide (NO_2^*). The light emitted during relaxation of the metastable NO_2^* is then amplified by a photomultiplier tube (PMT) that is sensitive to long-wavelength light. A 650- to 900-nm bandpass filter eliminates chemiluminescent interference by unsaturated hydrocarbons, chlorine, and sulfur, all of which react with O_3 but emit light of shorter wavelengths. The principle of operation of a C/CL nitrogen analyzer (Antek Instruments, Inc., Houston TX) is summarized in Figure 1.

A method for total nitrogen that is rapid, reproducible, and can be automated has tremendous advantages compared with the wet-chemical Kjeldahl method. The question of accuracy, however, is difficult to address. How do results from C/CL compare with those from Kjeldahl analyses for determination of nitrogen? Snodgrass (1981) reports that the sum of TKN and NO_3-N from fertilizer processing wastewater equals the total nitrogen (TN) yielded by

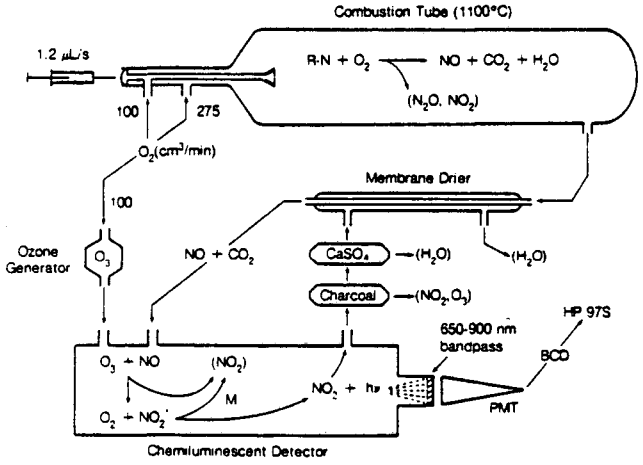

Figure 1. Reaction schematic of the Antek total-nitrogen analyzer, model #703C (XBL 8312-6910).

C/CL analysis. Similarly, Clifford and McGaughey (1982) report excellent agreement between C/CL and wet-chemical results for wastewater samples. For aqueous biological and clinical samples (rat urine and human urine and feces), Ward et al. (1980) find no significant difference between the C/CL method and a Kjeldahl method that uses a mixed $CuSO_4/SeO_2$ catalyst. For the distillate fraction of shale oil, Drushel (1977) notes that C/CL results were approximately 10% higher than Kjeldahl results. He attributes this to incomplete recovery by the wet-chemical method for some of the refractory nitrogenous compounds in shale oil rather than to a fundamental problem with the C/CL method of analysis. In this paper, we present the results of work comparing TKN and C/CL for the recovery of nitrogen from pure compounds and oil shale process waters.

<u>Organic Nitrogen by Combustion/Chemiluminescence</u>

In contrast to total nitrogen analysis, the <u>direct</u> determination of <u>organic</u> nitrogen in aqueous samples has not been possible by the C/CL approach. With the C/CL method, organic nitrogen can only be determined by difference (the value for ammoniac nitrogen determined by a separate method is subtracted from the TN value). Since oil shale wastewaters generally contain orders of magnitude more ammoniac nitrogen than organic nitrogen, the compounded errors of two methods are amplified. A sample pretreatment method that could effect a physical separation of inorganic from organic nitrogen would allow for the direct analysis of either fraction for TN.

We have adapted a method (Daughton, Jones, and Sakaji 1982) that employs the principles of reverse-phase chromatography to rapidly separate most of the organic nitrogen from the large amount of ammonia in oil shale process waters. This method, reverse-phase fractionation (RPF), is summarized in Figure 2. Disposable cartridges containing C_{18}-bonded silica are activated with methanol. The wastewater sample is applied to the cartridge, which is then rinsed with a small volume of water. Polar compounds are not retained; they pass through with the aqueous effluent (hydrophilic fraction; HpF). Nonpolar compounds are retained; they can be eluted with methanol (lipophilic fraction; LpF). The HpF contains ammonia, nitrate and nitrite salts, and polar organic nitrogen compounds (e.g., hydroxylated pyridines and nitriles). Alkylated pyridines, quinolines, and other nitrogenous heterocycles and aromatic amines reside in the methanolic LpF. The use of RPF allows approximately 120 samples to be prepared and analyzed for organic nitrogen in eight hours; the analysis of each sample only requires about 90 seconds. In contrast, five hours are required for analysis of nine samples using the Kjeldahl method with a 12-place digestion/distillation unit and automated titration. A detailed report on theory, statistical evaluation, and operator's protocols for C/CL and Kjeldahl analysis is in preparation (Jones, Harris, and Daughton 1984).

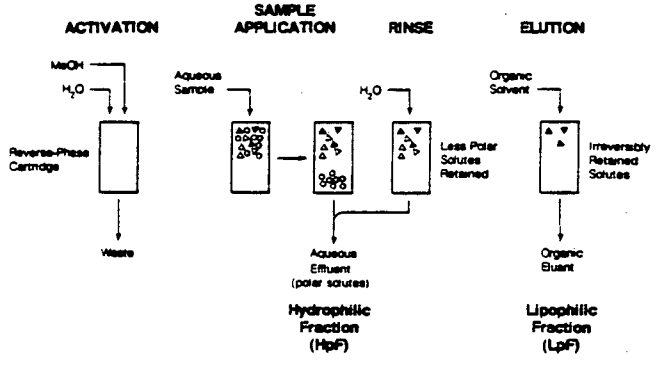

Figure 2. RPF scheme for separation of aqueous-waste solutes into hydrophilic (HpF) and lipophilic (LpF) fractions. Solutes belonging to the HpF are represented by (○). Solutes belonging to the LpF are represented by triangles; those which are irreversibly retained are represented by (▲) (XBL 843-1090).

MATERIALS, METHODS, AND EXPERIMENTAL DESIGN

An Antek nitrogen analyzer (model #703C) was used for the determination of nitrogen by C/CL. The instrument and principles of operation are discussed above. The nitrogen analyzer was interfaced with an

Hewlett-Packard (HP 97S) calculator that registered the integrated detector output (when stabilized) 50 seconds after sample injection. Values (slope and y-intercept) for the ammonium sulfate standard curve (J.T. Baker, Phillipsburg, NJ; 20 to 100 mg-N/L) and sample dilution factor were stored in the calculator memory; the nitrogen value for a sample was interpolated from the standard curve. All statistical analyses were based on the appropriate sections in Rohlf and Sokal (1969) and Sokal and Rohlf (1969).

For all Kjeldahl analyses, the ASTM recommended procedure (ASTM 1980) using either the digestion solution or Kel-Pak alternative was followed. Carbon content of 3,5-dimethylpyrazole was determined by the UV-persulfate oxidation/coulometric titration method (Langlois et al. 1984). Detailed operating protocols for the C/CL nitrogen methods are in preparation (Jones, Harris, and Daughton 1984).

To investigate the effects of solvents on C/CL recovery of nitrogen, standard curves between 20 and 100 mg-N/L were produced for 2,4,6-trimethylpyridine in either nanograde toluene or ASTM Type I water, ammonium sulfate in water, and 9-methylcarbazole in toluene. These solutions were prepared from 1 000 mg-N/L stock solutions by dilution in Class A 10-mL volumetric flasks.

The nitrogen compounds used in the pure compound and comparison studies were of the highest grade commercially available (manufacturers listed in Table I). Each of 52 compounds was placed in a Class A volumetric flask (25- to 100-mL) and weighed using a semi-micro analytical balance (model HL 52, Mettler Instrument Corp.). The amount of each compound was chosen to yield standard solutions of approximately 80 mg-N/L. The solutions were made to volume using either ASTM Type I water or appropriate solvent (4,4'-azoxyanisole, 1,5-dimethyltetrazole, 2,5-dimethyl-1,3,4-thiadiazole, indazole, m-nitrophenol, o-nitrophenol, p-nitrophenol, 6-nitroquinoline, and quinoline in HPLC grade methanol; carbazole, indole, isoquinoline, and 9-methylcarbazole in nanograde toluene). For the TKN analyses of 4-amino-2,3-dimethyl-2-phenyl-3-pyrazolin-5-one, 3,5-dimethylpyrazole, pyrazole, cyanuric acid, and nicotinic acid, 1.5-mL samples were withdrawn from 1 000 mg-N/L stock solutions and added directly to each Kjeldahl flask. Stock solutions and diluted samples were stored at 4°C in glass vials with Teflon-lined screw caps. Three single-operator replicates of the 52 compounds were analyzed by C/CL.

Table I. Sources of Nitrogen Heterocycles[1]

Alfa Products: Danvers, MA
piperidine (98%)

Aldrich: Milwaukee, WI
4,4'-azoxyanisole (NA[2])
2,3-dimethyl-1-(4-methylphenyl)-3-pyrazolin-5-one (99+%)
3,5-dimethylpyrazole-1-carboxamide (NA)
1,5-dimethyltetrazole (97+%)
2,5-dimethyl-1,3,4-thiadiazole (99%)
2-hydroxy-6-methylpyridine (97%)
2-hydroxypyridine (97%)
3-hydroxypyridine (97%)
imidazole (99%)
indazole (98%)
6-nitroquinoline (98%)
piperazine (99%)
pyrazole (98%)
pyridazine (97%)
pyrazine (99+%)

J.T. Baker: Phillipsburg, NJ
acetonitrile (HPLC grade)
diethanolamine (99.9%)
potassium nitrate (AR grade)

Burdick & Jackson: Muskegon MI
N-N-dimethylformamide (HPLC grade)

Calbiochem-Behring: La Jolla, CA
nicotinic acid (NA)

Carnegie-Mellon University: Pittsburg, PA
9-methylcarbazole (NA)

Chem Service: West Chester, PA
benzimidazole (NA)
carbazole (99+%)
cyanuric acid (NA)
3,5-dimethylpyrazole (99%)
2,4-dimethylpyridine (NA)
2,6-dimethylpyridine (NA)

Chem Service: West Chester, PA (cont.)
indole (99+%)
isoquinoline (NA)
2-methylpyrazine (99%)
2-methylpyridine (NA)
3-methylpyridine (NA)
4-methylpyridine (99%)
pyridine (99%)
quinoline (NA)
2,4,6-trimethylpyridine (99%)

Eastman Organic Chemicals: Rochester, NY
m-nitrophenol (NA)
o-nitrophenol (NA)
p-nitrophenol (98%)

Fisher: Fair Lawn, NJ
glycine (NA)

Fluka AG: Buchs, Switzerland
5-ethyl-2-methylpyridine (NA)

Hellige: Garden City, NJ
nitrite salt solution (50 mg-N/L)
urea (NA)

Mallinckrodt: St. Louis, MO
4-amino-2,3-dimethyl-2-phenyl-3-pyrazolin-5-one (NA)

Matheson Coleman & Bell: East Rutherford, NJ
ethylenedinitrilotetra-acetic acid (NA)

NOAH Chemical: Farmingdale, NY
3-ethyl-4-methylpyridine (NA)
4-ethyl-3-methylpyridine (NA)
2-ethylpyridine (NA)
3-ethylpyridine (NA)
4-ethylpyridine (NA)
2-n-propylpyridine (NA)
2,3,6-trimethylpyridine (NA)

[1] purities given in parentheses
[2] not available

Duplicate samples of 17 compounds (listed in Table II) were analyzed for nitrogen content by the Kjeldahl method, and their TKN values were compared with the results from C/CL.

Table II. Percent Recoveries of Nitrogen from 17 Compounds Using the Total Kjeldahl Nitrogen (TKN) Method

Compound	% theoretical-N
pyridine	81
nicotinic acid	99
piperidine	87
pyridazine	94
4-amino-2,3-dimethyl-2-phenyl-3-pyrazolin-5-one	53
2,3-dimethyl-1-(4-methylphenyl)-3-pyrazolin-5-one	79
pyrazole	15
3,5-dimethylpyrazole	17
indazole	46
1,5-dimethyltetrazole	46
2,5-dimethyl-1,3,4-thiadiazole	5
imidazole	25
cyanuric acid	102
m-nitrophenol	57
o-nitrophenol	< 1
p-nitrophenol	51
4,4'-azoxyanisole	72

To determine if oil shale process waters exert a matrix effect, a standard additions study was designed to compare the TKN and TN values. A composite sample of unfiltered oil shale process waters (equal volumes of nine process waters listed in Table III) was diluted 1:200 so that the total nitrogen concentration was approximately 35 mg/L. Nicotinic acid (3-pyridinecarboxylic acid), a nonhygroscopic compound that is reported to be one of the more difficult compounds to recover by Kjeldahl digestion (Bowman and Delfino 1982), was added to samples of diluted composite water so that the nicotinic acid concentrations were 15, 35, and 55 mg-N/L. The final TN concentrations of these spiked samples were 50, 70, and 90 mg-N/L.

Table III. Determination of Total Nitrogen in Oil Shale Process Waters: Combustion/Chemiluminescence (TN) versus Kjeldahl (TKN)

Process Water	TN	rsd	TKN	rsd	(% diff)[1]
Paraho	28 805	3.5	29 661	1.9	2.9
150-Ton	10 084	1.3	10 453	1.2	3.5
Oxy-6 GC	6 886	3.5	6 985	1.9	1.4
Composite	6 712	2.3	7 108	1.3	5.6
S-55	4 196	2.1	4 379	2.3	4.2
Omega-9	3 574	1.9	3 698	1.3	3.4
TOSCO HSP	2 826	2.6	2 809	1.7	-0.6
Geokinetics	1 844	2.1	1 826	0.5	-1.0
Oxy-6 RW	1 313	1.8	1 349	0.9	2.7
Rio Blanco sour	1 133	3.4	1 074	1.5	-5.5

[1] [(TKN - TN)/(TKN)] X 100

To compare TN values for different retort waters and to determine method precision, samples of nine oil shale process wastewaters and a composite sample (Table III) were filtered (0.4-μm pore-diameter polycarbonate membranes) under pressure and diluted to yield concentrations of between 30 and 75 mg-N/L; the origin of these waters is described in Langlois et al. (1984). These samples were stored in a manner identical to the pure compound standards. Ten single-operator replicates of each process water sample were analyzed for nitrogen by C/CL, and three single-operator replicates were analyzed for total nitrogen by the Kjeldahl method.

The separation of lipophilic organic solutes from ammonia in the parent process water was accomplished by RPF (Daughton, Jones, and Sakaji 1982). The standard fractionation procedure was modified slightly; all of the aqueous effluent (sample and rinse) was collected as HpF, and the LpF was eluted with methanol followed by tetrahydrofuran. Nine oil shale wastewaters and a composite water were filtered and fractionated. The TN content of both the LpF and HpF was determined by C/CL in triplicate for each of three replicate sample fractionations. To determine the effectiveness of RPF in separating organic nitrogen from inorganic nitrogen species, the LpF-TN value of each process water was compared with the results from triplicate determinations of OKN for each sample.

RESULTS AND DISCUSSION

Solvent Effects

Water has been reported to depress detection of nitrogen with C/CL by lowering the burner-tip temperature, quenching chemiluminescence, and contributing to 2- and 3-body reactions. An 1100°C furnace mitigates the effect of burner-tip temperature depression by aqueous samples. The Antek 703C nitrogen analyzer has a membrane dryer that eliminates water from the gas stream and therefore minimizes quenching. The slope of standard curves between 20 and 100 mg-N/L (attenuation = 20) for 2,4,6-trimethylpyridine in either toluene or water were nearly identical: 6.07×10^6 and 6.14×10^6 counts/mg-N, respectively. Two other standard curves obtained at the same time (ammonium sulfate in water and 9-methylcarbazole in toluene) also had slopes that were virtually indistinguishable from those of 2,4,6-trimethylpyridine (6.08×10^6 and 6.07×10^6 counts/mg-N, respectively). Compounds dissolved in methanol (quinoline and 6-nitroquinoline) did not exhibit an enhanced response when compared with an ammonium sulfate standard in water (Fig. 3). These results indicate that water probably does not interfere with the combustion of the sample or with the detection of nitrogen by chemiluminescence and that either toluene or methanol can be used interchangeably with water, as required by the solubility of the analyte.

Pure Compounds: Recovery Study

To ensure that the C/CL system would be applicable to detection of nitrogen in oil shale process waters, the recovery of nitrogen was determined for compounds reported to be resistant to Kjeldahl digestion (pyridines and quinolines) and compounds reported to be prevalent in process waters (alkyl-substituted pyridines). The majority of the 52 compounds tested yielded 90% to 110% of their theoretical nitrogen contents. Compounds that contained the pyrazole nucleus, however, exhibited exceptionally low recoveries. Less than 15% of the nitrogen was recovered from pyrazole (Fig. 3), and the recovery of nitrogen did not exceed 50% from other com-

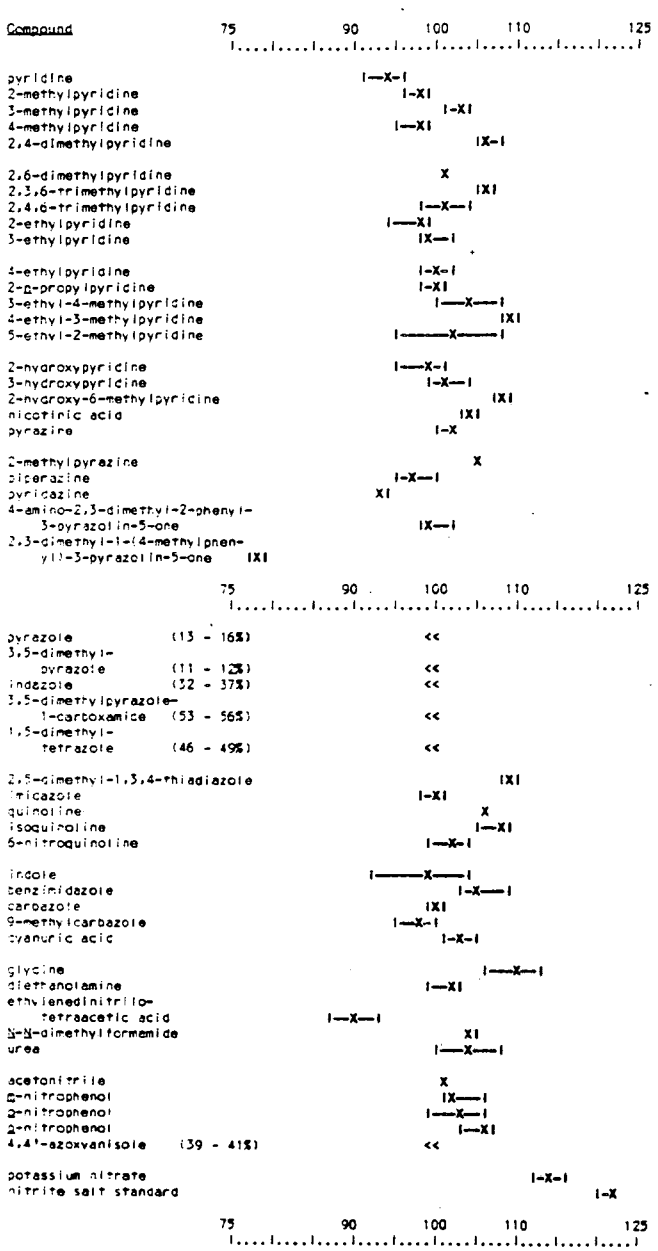

Figure 3. Percent recovery of nitrogen from 52 standard solutions by C/CL nitrogen analysis using an ammonium sulfate standard curve (mean = X) (range = I—I) (XBL 8310-12246).

pounds with the pyrazole nucleus (e.g., indazole and tetrazole). The relationship of chemical structure to nitrogen recovery is illustrated in Figure 4.

Another compound that yielded incomplete recovery of nitrogen was 4,4'-azoxyanisole. Diazo compounds have been reported to be somewhat resistant to C/CL nitrogen analysis presumably because of the liberation of the N=N moiety as molecular nitrogen. Inorganic nitrate and nitrite salts yielded enhanced

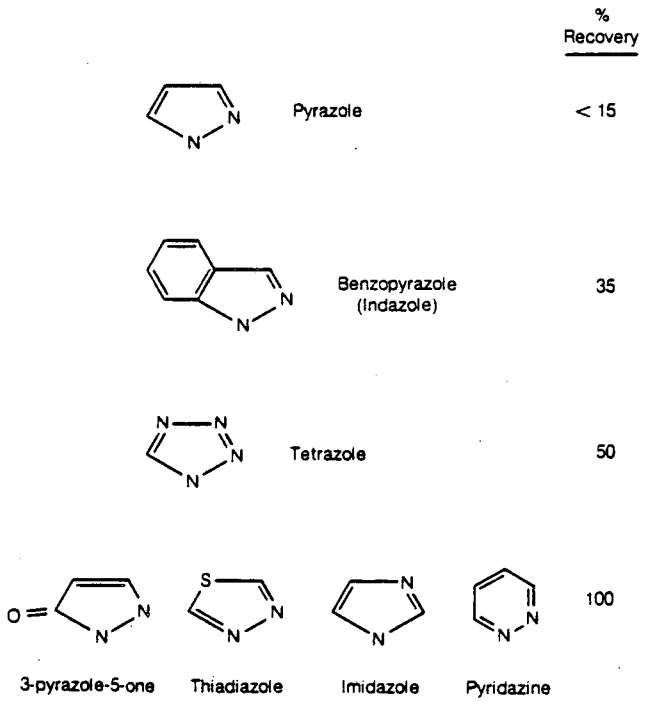

Figure 4. Summary of percentage nitrogen recoveries from pyrazole-related compounds (XBL 8312-6909).

responses; 114% and 122% nitrogen were recovered, respectively. Inorganic nitrogen oxides and pyrazoles are present, however, at extremely low concentrations in oil shale process wastewaters and therefore would not be expected to interfere with the recovery of nitrogen by C/CL. The application of C/CL to the determination of nitrogen in oil shale wastewaters seems justified.

Only 3 of 17 compounds tested yielded greater than 90% recovery of their theoretical nitrogen contents using the TKN method (Table II). In contrast to the reported resistance of nicotinic acid to Kjeldahl digestion, 99% of the theoretical nitrogen content was recovered from this compound. Similarly, pyridazine and cyanuric acid yielded greater than 90% of their theoretical nitrogen values. Compounds containing the pyrazole nucleus and tetrazole, however, yielded only 15% to 79% of their theoretical nitrogen values. Imidazole and 2,5-dimethyl-1,3,4-thiadiazole yielded only 5% to 25% of their theoretical nitrogen. These results are not surprising because the N-N linkage in pyrazolones and similar compounds has been reported as extraordinarily resistant to Kjeldahl digestion (Lennox and Flanagan 1982). None of the three nitrophenols yielded its theoretical nitrogen content. The Kjeldahl method of nitrogen analysis should be applied with caution to

aqueous waste streams, such as oil shale wastewaters, that contain some of these refractory classes of compounds.

Matrix Effects: Standard Additions

The addition of nicotinic acid to retort water to give various known concentrations was used to detect matrix effects (e.g., enhanced or depressed responses). The recovery of nicotinic acid spikes from diluted composite samples ranged from 98% to 103% for C/CL and from 102% to 104% for the Kjeldahl method. The x-intercept values were within 5% of the respective zero-spike values indicating that matrix effects were at worst minimal. For the diluted samples, the x-intercept for the C/CL method was 36.52 mg-N/L, and the zero-spike value was 38.55 mg-N/L. The x-intercept for the Kjeldahl method was 35.51 mg-N/L, and the zero-spike value was 34.27 mg-N/L. The coefficient of determination (r^2) values for both methods exceeded 0.9990.

Total Nitrogen: Comparison of C/CL and Kjeldahl

The values for TN by C/CL were compared with those for TKN for nine oil shale process waters and a composite water. The results are presented in Table III and Figure 5. The values obtained by the two

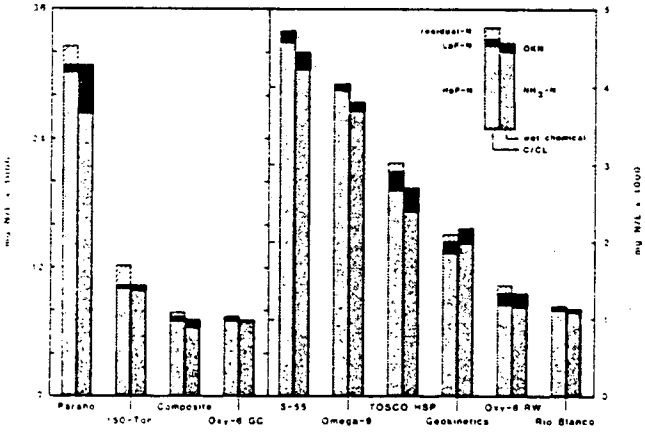

Figure 5. Nitrogen values for oil shale process waters obtained by C/CL and Kjeldahl. For each pair of bars, the top of the left member is total nitrogen (TN) as determined by C/CL and the top of the right member is total Kjeldahl nitrogen (TKN) as determined by wet-chemical analysis. The C/CL nitrogen values for the reverse-phase fractions, HpF and LpF, are estimators of NH_3-N and organic Kjeldahl nitrogen (OKN), respectively. The cross-hatched areas are residual-N, that portion of the TN not accounted for by the sum of the two fractions; for S-55, the total nitrogen value was 111 mg-N/L less than the sum (XBL 8310-12247).

methods agreed remarkably well. The difference in recovery of nitrogen by the two methods ranged from -5.5% to +5.6%. The relative standard deviation (rsd) values for TN were less than 3.5%, and those for TKN were less than 2.5%. To determine if a significant difference existed between the two methods, a two-way analysis of variance (anova) was conducted using the first three TN determination values for each sample and the triplicate TKN results. There was no significant difference ($P>0.10$) between the two nitrogen methods, $F_s<F_{.10}$ ($2.30<2.84$), although there was a significant interaction effect between methods and wastewaters, $F_s>F_{.005}$ ($3.90>3.22$). The results of Tukey's test for nonadditivity indicated that an insignificant portion ($P>0.10$) of the interaction was nonadditive; therefore the assumptions of the anova were not violated. This interaction effect was most likely a result of the wide range of nitrogen values among the waters.

Organic Nitrogen: Comparison of C/CL and Kjeldahl

Organically bound nitrogen is generally quantitated by using a combination of wet-chemical methods (e.g., ammonia predistillation followed by Kjeldahl digestion for organic Kjeldahl nitrogen; or total Kjeldahl digestion and a separate ammonia analysis). The TKN and OKN values for the nine oil shale wastewaters and a composite sample are given in Table IV.

Table IV. Total Kjeldahl Nitrogen (TKN) and Organic Kjeldahl Nitrogen (OKN) for Nine Oil Shale Process Waters and a Composite Water

Process Water	TKN	rsd (%)	OKN	rsd (%)	% OKN[1]
Paraho	29 661	1.9	4 299	1.8	14.5
150-Ton	10 453	1.2	541	3.4	5.2
Oxy-6 GC	6 985	1.9	21	1.4	0.3
Composite	7 108	1.3	652	1.0	9.2
S-55	4 379	2.3	372	0.9	8.5
Omega-9	3 698	1.3	112	0.9	3.0
TOSCO HSP	2 809	1.7	305	1.2	10.9
Geokinetics	1 826	0.5	194	3.4	10.6
Oxy-6 RW	1 349	0.9	183	3.0	13.6
Rio Blanco sour	1 074	1.5	14	4.8	1.3

[1] [(OKN)/(TKN)] X 100

The percentage of TKN accounted for by OKN was highest for Paraho (14.5% of TKN). The average organic nitrogen content of the nine waters was 7.7% of TKN, and that of the composite sample was 9.2% of TKN. Oxy-6 gas condensate (GC), a condensate of process off-gases collected simultaneously with Oxy-6 retort water (RW), had one of the lowest concentrations of OKN (21 mg-N/L).

To test the effectiveness of the RPF method for separating inorganic from organic nitrogen, we

analyzed the unfractionated filtrates and two fractions (HpF and LpF) of nine oil shale process waters and a composite water for TN using the prescribed C/CL procedure. These results were compared with those from the respective wet-chemical method (OKN and titrimetric ammonia-N for LpF-TN and HpF-TN, respectively). The results of these analyses are presented in Figure 5.

For all of the process waters analyzed, from 8% to 24% of the organic nitrogen was sufficiently polar to be collected with the ammonia in the hydrophilic fraction. The nonpolar nitrogen recovered by LpF-TN was from 48% to 100% of the respective OKN concentrations for all but one of the waters, and the average LpF-TN:OKN ratio was 0.67. The nitrogen content of the LpF was therefore an underestimator of the OKN. For all but two of the wastewaters, the TN determined on the unfractionated sample exceeded the sum of the LpF-TN and HpF-TN as well as the sum of NH_3-N and OKN. This indicated in the first instance that a portion (residual-N in Figure 5) of the organic nitrogen was irreversibly retained by the C_{18} stationary phase. In the second instance, it indicated that a portion of the nitrogen was unrecovered by the Kjeldahl procedure; some of the OKN was either steam distilled or hydrolyzed to ammonia prior to OKN digestion, or a portion of the solutes was refractory to Kjeldahl digestion. Even though organic nitrogen may be incompletely recovered by the RPF method, LpF-TN is a reliable indicator of nonpolar organic nitrogen and has been successfully applied to yield valuable information about the fate of organic nitrogen solutes during biotreatment (Healy et al. 1983).

Cost Comparison

A cost comparison of the macro-Kjeldahl apparatus and the Antek 703C nitrogen analyzer showed that the capital expense of the Kjeldahl apparatus and flasks was approximately half that of the Antek nitrogen analyzer and syringe drive ($7,800 vs. $14,800). The yearly costs of expendables were approximately equal for the two methods. Assuming two full-rack Kjeldahl digestions per day, 100 days per year, the acid, base, and digestion reagents would cost approximately $1600. For the nitrogen analyzer, replacement combustion tubes, syringes, scrubbers, septa, and high-purity oxygen for 100 days of operation would be approximately $1950 per year. Neither of these estimates includes the electrical demand of the units. Operator's time for the C/CL method (per sample) is considerably less than for the Kjeldahl method.

SUMMARY

Wastewaters from the recovery of shale oil are highly contaminated; organic nitrogen compounds (i.e., nitrogenous heterocycles and aromatic amines) have been postulated as responsible for a large portion of the biorefractory solutes. Total Kjeldahl nitrogen and organic Kjeldahl nitrogen, the standard methods for quantifying nitrogen in agricultural and biological wastewaters, are extremely time-consuming procedures, and nitrogenous heterocycles are notoriously resistant to the Kjeldahl digestion step. Total nitrogen as determined by combustion at 1100°C followed by excitation of the by-products with ozone to an electronically excited species (NO_2^*) and chemiluminescent detection was demonstrated to recover a wide range of nitrogenous heterocycles. There was no statistically significant difference between TKN and TN for nine oil shale wastewaters.

Separation of ammonia from the aqueous sample matrix by reverse-phase fractionation was evaluated for its ability to broaden the scope of C/CL analysis. Total nitrogen values for the RPF nonpolar fraction of oil shale wastewaters revealed that this method of solute separation followed by analysis with C/CL may be among one of the most rapid methods available for estimating organic nitrogen.

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