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# Determination of Alkyl Anilines and Alkyl Pyridines in Solvent Refined Coal Distillates and Aqueous Extracts by Gas Chromatography/Mass Spectrometry

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Derivatization with acetic anhydride in aqueous media coupled with capillary gas chromatography/mass spectrometry was used to distinguish alkyl anilines from alkyl pyridines. By use of this approach aniline, C-1 anilines, and C-2 anilines, as well as lesser quantities of C-2 pyridines and C-3 pyridines, were positively identified in a solvent refined coal (SRC)-II blended distallate and in an aqueous extract of the distillate. The extraction procedure and acetylation conditions employed were examined in detail and found suitable for quantitative analysis when combined with capillary gas chromatography. The SRC-II blended distillate contained 8200-9025 µg/mL anilines and 1335 µg/mL pyridines. Distilled water equilibrated with the distillate (1:100, SRC-II:H2O) contained 65.9–78.9  $\mu$ g/mL anilines and 5.6  $\mu$ g/mL pyridines.

As the synthetic fuels industry develops, environmental studies are needed to provide information for the growth of an environmentally acceptable industry. Of particular concern is the relatively high quantity of nitrogen- and oxygen-containing compounds found in coal-derived liquids (1) and the fate of such components if spilled into the environment. Many of these polar water soluble species, such as anilines and phenols, are toxic and have a high potential for environmental mobility, thus posing a threat to surface and ground waters. In aquatic toxicity studies of aqueous extracts of an SRC-II distillate for example, phenols were found to contribute to more than 50% of the organic carbon in the extracts (2). In order to accurately assess the potential hazards associated with a spill of coal-derived liquids, analytical methodology to characterize the polar constituents of these liquids and to follow these compounds through environmental systems must be available.

In this report an analytical approach based on chemical derivatization with acetic anhydride in aqueous media followed by capillary gas chromatography (GC) and capillary gas chromatography/mass spectrometry (GC/MS) is presented for the identification and quantitation of trace quantities of alkyl anilines and pyridines in SRC-II distillates and aqueous solutions contacted by SRC-II liquids. Both anilines and pyridines have been previously analyzed in coal-derived liquids by GC/MG (3-5). However, the similarity of the electron impact mass spectra of alkyl anilines and pyridines and the lack of a complete set of standard compounds prompted the development of alternative analytical method that could unambiguously differentiate anilines from pyridines. Derivatization of alkyl anilines with acetic anhydride occurs rapidly in aqueous media and results in acetanilide derivatives which are easily distinguished from the underivatized alkyl pyridines by GC or GC/MS. In addition to providing a useful qualitative tool, the acetylation approach was found to be quantitative and was used for the measurement of alkyl anilines and pyridines in an SRC-II blended distillate and aqueous extracts of the distillate. The approach presented is thought to have broad applicability and to be useful for distinguishing primary aromatic amines from nitrogen heterocycles.

## EXPERIMENTAL SECTION

Chemicals. All solvents used were Burdick and Jackson distilled in glass. Standard pyridines, anilines, and acetanilides were purchased from Pfaltz and Bauer and Aldrich Chemical Co. 4-Ethylacetanilide and 2,4,5-trimethylacetanilide were synthesized as described below.

Synthesis of Acetanilides. An aqueous solution of 4ethylaniline (6.2 g), 0.42 M (103 mL), was warmed to 50 °C, acetic anhydride (6 mL) was added followed by 2.4 M aqueous sodium acetate (25 mL). The mixture was stirred and then cooled in an ice bath until the product crystallized. The acetanilide was recrystallized twice from water/ethanol. 2,4,5-Trimethylacetanilide was prepared in the same manner and recrystallized twice from ether/ethanol. The mass spectra and infrared spectra of both compounds were consistent with the desired products.

SRC-II Distillate. The SRC-II distillate used throughout this study is a blend of middle and heavy distillates (2.9:1.0) produced at the SRC-II pilot plant at Fort Lewis, WA, operated by the Pittsburg & Midway Coal Mining Co. The blend is not necessarily representative of a future commercial product. An aqueous extract of this blend was prepared by mixing 1 part SRC-II blended distillate with 100 parts water (v/v) for 24 h. After allowing the SRC to settle, the aqueous layer was separated and passed through a glass wool plug. The aquatic toxicity of aqueous extracts of the SRC-II blended distillate, prepared in a similar manner, have been studied extensively at the Pacific Northwest Laboratories (2).

Capillary Gas Chromatography (GC) and Capillary Gas Chromatography/Mass Spectrometry (GC/MS). Gas chromatographic analyses were performed on a Hewlett-Packard 5880A equipped with flame ionization (FID) and nitrogen/ phosphorus (N/P) detectors. A 60-m SP2100 capillary column (J&W Scientific) was used for all experiments with the following temperature program: initial oven temperature at 75 °C for 4



Figure 1. Gas chromatograms of acetylated nitrogen compounds from SRC-II blended distillate: (A) N/P detector, (B) FID detector; (1) acetanilide, (2) 2-methylacetanilide, (3) C-2 acetanilide, (4) 3-methylacetanilide, (5) 4-methylacetanilide, (6), (7), (9-12) C-2 acetanilide, (8) C-2 acetanilide and C-3 acetanilide, (13) C-3 acetanilide, (14) benzanilide.

min, increased to 250 °C at a rate of 4 °C/min, and then held at 250 °C for 15 min.

GC/MS analyses were performed on a Hewlett-Packard 5985 system with a 7900/7920 multidisk drive and operating in the electron impact mode. All GC/MS runs were carried out in the splitless mode using the temperature program described above. A 50-m methyl silicone fused silica capillary column (Hewlett-Packard) was used with the column outlet running directly into the mass spectrometer source.

Acetylation Procedure. The SRC-II aqueous extract (50 mL) was adjusted to pH 12 with 5 M NaOH and extracted twice with  $CH_2Cl_2$  (1 × 50 mL, 1 × 25 mL). The  $CH_2Cl_2$  extracts were combined, back-extracted with 1 M HCl (40 mL) and the HCl extract, and then adjusted to pH 12 with 5 M NaOH. Acetic anhydride (0.5 mL) was added and the mixture shaken and left standing at room temperature for 5–10 min. The solution was extracted twice with  $CH_2Cl_2$  (1 × 20 mL, 1 × 10 mL), whereupon the combined  $CH_2Cl_2$  extracts were dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under a stream of nitrogen. If alkyl pyridines are to be analyzed, the reaction mixture must be readjusted to a basic pH prior to extraction with  $CH_2Cl_2$  to obtain favorable extraction efficiencies.

Extraction of organic nitrogen compounds from the SRC-II blended distillate was accomplished by dissolving the distillate (0.2 mL) in CH<sub>2</sub>Cl<sub>2</sub> (75 mL) and extracting with 1 M HCl (40 mL). The HCl extract was then adjusted to pH 12 with 5 M NaOH and acetic anhydride (0.5 mL) added and left standing at room temperature for 5–10 min after shaking. The solution was extracted twice with  $CH_2Cl_2$  (1 × 20 mL, 1 × 10 mL) and then the combined extract dried over  $Na_2SO_4$  and concentrated under a stream of nitrogen.

Individual compounds were identified by GC and GC/MS. All quantitative results were obtained by measurement of GC peak areas using the internal standard method with benzanilide as the internal standard. When GC analysis was performed in the splitless mode or when the N/P detector was used, the concentrated  $CH_2Cl_2$  extract was replaced by heptane.

## **RESULTS AND DISCUSSION**

The extraction procedure utilized in this study yielded a nitrogen-enriched fraction when applied to the SRC-II blended distillate and an aqueous extract of this distillate. Gas chromatographic analysis with FID and N/P detectors of an acetylated SRC-II extract illustrates the extent of nitrogen enrichment (Figure 1). GC/MS analysis of the nitrogen fractions showed a number of major components with mass spectra consistent with an alkyl pyridine or alkyl aniline structure. However, the distinction between a pyridine or aniline could not be made on the basis of mass spectra because the electron impact fragmentation patterns are too similar,

## Table I. Percent Recovery of Anilines as Acetanilide Derivatives $^a$

compound	recovery A	recovery B	recovery C
aniline	44 (8)	50 (3)	71 (2)
2-methylaniline	47 (8)	55 (3)	69 (3)
4-methylaniline	54 (8)	62 (3)	77(2)
2,6-dimethylaniline	46 (7)	58 (3)	70 (2)
2,4-dimethylaniline	55 (7)	63 (3)	79 (3)
4-ethylaniline	60 (7)	77 (12)	78 (2)
2,4,5-trimethylaniline	70 (6)	77 (2)	77(2)

<sup>a</sup> (A) recovery (standard deviation) (n = 4) from 50 mL of H<sub>2</sub>O. (B) recovery (standard deviation) (n = 4) from 75 mL of CH<sub>2</sub>Cl<sub>2</sub>. (C) recovery (standard deviation) (n = 4) from 50 mL of acetylation mixture.

 
 Table II. Recovery of Standard Acetanilides Added to the Acetylation Mixture

compound	% recovery <sup>a</sup>
acetanilide	71(1)
2-methylacetanilide	76 (5)
4-methylacetanilide	81 (4)
2,6-dimethylacetanilide	72(4)
2,4-dimethylacetanilide	94 (6)
4-ethylacetanilide	80 (6)
2,4,5-trimethylacetanilide	97 (3)

<sup>a</sup> Recovery (standard deviation) (n = 4) from 50 mL of aqueous NaOH/acetic anhydride mixture.

nor could it be made on the basis of GC retention data because of the similarity in boiling points. The absolute characterization of individual alkyl pyridines or alkyl anilines was also hampered by the large number of possible alkyl isomers and the absence of a complete set of standards. The problems associated with the identification and quantitation of these compound types were circumvented by derivatizing the anilines with acetic anhydride in aqueous media followed by GC and GC/MS analysis. The resulting acetanilide derivatives had GC retention times that were significantly longer than the alkyl pyridines (Figure 2) and had mass spectral fragmentation patterns that were readily distinguishable from the alkyl pyridines. The electron impact mass spectra of the acetylated anilines contained a prominent  $(M - 42)^+$  ion corresponding to the loss of ketene as well as a relatively intense molecular ion. Reaction with acetic anhydride is rapid requiring only several additional minutes of sample processing time and no additional sample manipulations. By use of the acetylation approach, aniline, 2-, 3- and 4-methylaniline, and a number of C-2 anilines and C-3 anilines were identified in the SRC-II blended distillate and an aqueous extract of the distillate (Figure 3).

Since the acetylation of anilines with acetic anhydride was facile and could provide a useful tool for the quantitative analysis of anilines, several important reaction parameters were examined. Recoveries for a number of standard anilines were measured at the level of  $1-2 \mu g/mL$  aniline at various stages of the acetylation procedure and are presented in Table I. The overall recoveries of anilines carried through the derivatization procedure were greater than 40% from distilled water and greater than 50% from methylene chloride.

The low recoveries obtained are probably due to the cumulative losses incurred at the various extraction steps (Table I). When the recoveries of acetanilide standards added to the acetylation reaction mixture were determined, extraction losses as high as 30% were found (Table II). Furthermore, when a number of alkyl anilines were carried through the acetylation procedure, unreacted anilines were not detected during GC analysis of the resulting acetanilides. Recoveries might have



Figure 2. (A) Chromatogram of standard mixture of pyridines and anilines: (1) 2,5-dimethylpyridine, (2) aniline, (3) 3,4-dimethylpyridine, (4) 2-methylaniline, (5) 4-methylaniline, (6) 4-ethyl-3-methylpyridine, (7) 2,6-dimethylaniline, (8) 3,4-dimethylaniline, (9) 4-ethylaniline, (10) 2,4,5-trimethylaniline, (11) benzanilide. (B) Chromatogram of acetylated standard mixture of anilines and pyridines: (1) 2,5-dimethylpyridine, (2) 3,4-dimethylpyridine, (3) 4-ethyl-3-methylpyridine, (4) acetanilide, (5) 2-methylacetanilide, (6) 2,6-dimethylacetanilide, (7) 4-methylacetanilide, (8) 2,4-dimethylacetanilide, (9) 4-ethylacetanilide, (10) 2,4,5-trimethylacetanilide, (11) benzanilide.



Figure 3. Gas chromatograms of organic nitrogen compounds from SRC-II aqueous extract: (A) underivatized nitrogen fraction, (1) C-2 pyridine, (2) C-2 pyridine, (3) C-2 pyridine, (4) aniline, (5) C-3 pyridine, (6) C-3 pyridine, (7) C-1 aniline, (8) C-1 aniline, (9) C-2 aniline, (10) C-2 aniline, (11) C-2 aniline, (12) C-2 aniline, (13) benzanlide; (B) acetylated nitrogen fraction, (1) C-2 pyridine, (2) C-2 pyridine, (3) C-2 pyridine, (4) C-3 pyridine, (5) C-3 pyridine, (6) acetanilide, (7) 2-methylacetanilide, (8) C-2 acetanilide, (9) 3-methylacetanilide, (10) 4-methylacetanilide, (11) C-2 acetanilide, (12) C-2 acetanilide, (13) C-2 and C-3 acetanilide, (14) C-2 acetanilide, (15) C-2 acetanilide, (16) C-2 and C-3 acetanilide, (17) C-2 acetanilide, (18) C-2 acetanilide, (19) C-3 acetanilide, (20) benzanilide.

been improved by the use of a solvent other than methylene chloride; however, the recoveries obtained were considered adequate and the use of a solvent more dense than water added to the convenience of the method.

A reaction time of about 5-10 min was optimum with no significant increase in recoveries at times of up to 45 min. One undesireable feature of the derivatization procedure is the need to adjust the 1 M HCl extract to pH 12 with sodium hydroxide. It would be preferable if the acetylation could be run in a buffered medium so as to facilitate the pH adjustment step. However, acetylation in sodium carbonate and acetate buffer (pH 4.7) resulted in drastically reduced yields.

Alkyl anilines in the SRC-II blended distillate and the SRC-II aqueous extract were quantitated by GC analysis of their acetanilide derivatives. Results of these analyses are

Table III.	Analysis <sup>a</sup> of Anilines in SRC-II Blended			
Distillate and Corresponding Aqueous Extract				

	SRC-II distillate		SRC-II aqueous extract	
compound	analysis I	analysis II	analysis I	analysis II
aniline 2-methylaniline 3-methylaniline 4-methylaniline C-2 aniline	$1170 \\ 2340 \\ 1735 \\ 400 \\ 2555$	$1025 \\ 2545 \\ 1660 \\ 445 \\ 3350$	$11.4 \\ 21.0 \\ 14.5 \\ 4.5 \\ 14.5 \\ 14.5$	$14.3 \\ 25.1 \\ 16.2 \\ 4.4 \\ 18.9$

Table IV. Percent Recovery of Alkyl Pyridines from Acetylation Procedure<sup>a</sup>

compound	recovery	recovery	recovery
	A	B	C
2,5-dimethylpyridine	$\begin{array}{c} 65 \ (4) \\ 65 \ (6) \\ e \ 65 \ (4) \end{array}$	79 (4)	91 (2)
3,4-dimethylpyridine		78 (2)	86 (4)
4-ethyl-3-methylpyridine		75 (4)	89 (3)

<sup>a</sup> (A) recovery (standard deviation) (n = 4) from 50 mL of  $\dot{H}_2 O$ . (B) recovery (standard deviation) (n = 4) from 75 mL of  $CH_2Cl_2$ . (C) recovery (standard deviation) (n =4) from 50 mL of acetylation mixture.

given in Table III for two sets of samples prepared and analyzed on different days. Standards were available for quantitation of acetanilide, 2-methylacetanilide, and 4methylacetanilide; however, the determination of 3-methylacetanilide was based on the 2-methyl and 4-methyl isomers. Quantitation of the C-2 acetanilides was based on data for 2,6-dimethylacetanilide and 2,4-dimethylacetanilide. A number of relatively small GC peaks were tentatively identified as C-3 acetanilides; however, these were not fully resolved from other components and were not quantitated. Several small C-2 acetanilide peaks were also excluded from quantitation due to inadequate resolution.

The alkyl pyridines are uneffected by the acetic anhydride treatment and can be recovered in high vields from the acetylation reaction medium (Table IV). The gas chromatographic behavior of the alkyl pyridines is markedly different from that of the acetanilides (Figure 2) and allows the simultaneous quantitation of these two compound classes. A number of compounds in the SRC-II distillate were tentatively identified as C-2 and C-3 pyridines based on their GC/MS data and the fact that they were not influenced by treatment with acetic anhydride. With 3,5-dimethylpyridine as a standard, the quantity of alkyl pyridines in the SRC-II distillate and the SRC-II aqueous extract was estimated. Concentrations of pyridines in the SRC-II blend were 975  $\mu$ g/mL C-2 pyridine and 360  $\mu$ g/mL C-3 pyridine. The SRC-II aqueous extract contained 3.9  $\mu$ g/mL C-2 pyridine and 1.7  $\mu$ g/mL C-3 pyridine.

In summary, the alkyl anilines have been shown to be the predominant monocyclic nitrogen compounds in the SRC-II blend examined. The toxicity of the anilines (6, 7) and their potential mobility indicate that the anilines should be considered in environmental fate studies of SRC products. The methodology developed is generally applicable and should prove useful for the routine trace analysis of aromatic amines in aqueous samples. The extension of this approach to higher molecular weight aromatic amines is now under investigation.

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## Determination of Lead in Aqueous Samples as the Tetramethyl Derivative by Atomic Absorption Spectrometry

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A new method for the determination of lead in aqueous samples is described. The method involves the extraction of Pb<sup>2+</sup> into chloroform as the dithlocarbamate complex followed by solvent evaporation and methylation of the residue with methyllithium to form tetramethyllead. The analyte vapor is then trapped on a short column of Porapak Q from which it is eluted into a quartz furnace atomic absorption detector. A relative standard deviation of 6.8% was obtained at the 50 ng/mL level. The working range extends from the detection limit of 5 ng to an upper limit of approximately 200 ng. The results of the analysis of lead-containing Environmental Protection Agency Water Pollution Quality Control Samples are reported.

Metal volatilization techniques provide a number of significant benefits in atomic absorption spectrometry. First, matrix effects can be circumvented. Generally, it is possible to selectively derivatize the analyte while leaving behind the interferences. Second, separation of the analyte from the solvent eliminates the expenditure of thermal energy upon solvent evaporation in contrast to direct aqueous aspiration. Third, due to the thermal instability (1) of many volatile metal-containing compounds (compared to their inorganic counterparts), decomposition to the free atoms is facile at relatively low flame or furnace temperatures. Because of the increase in free atom population, the enhancement of atomic emission, absorption, and fluorescence signals is expected. Finally, sensitivity improvement through preconcentration can be obtained when a trapping system is employed in connection with the volatilization scheme. In this manner it is feasible to measure very low analyte concentrations because the volatilized metal compound can be collected from a large solution volume.

A vapor generation technique that has not received significant consideration for many metals is the alkylation of the analyte to form an organometallic species. The alkylated derivatives of most post-transition metals and metalloids are both volatile and stable enough to be trapped and subsequently eluted into a suitable detection system (2). Because hydride generation techniques (3) cannot be applied to all metals, alkylation may be a possible alternative in many cases, despite the fact that most alkylating agents cannot be used directly with aqueous solutions. The metal whose alkylation has been investigated most thoroughly as an analytical approach is mercury. Mono- and dialkylmercury compounds

have been formed from inorganic species and separated by using gas chromatography (4, 5).

The phenylation of dithiocarbamate complexes has been used as a volatilization technique in the determination of As. Sb, Tl, Se, Te, Hg, Bi, and Sn by Schwedt et al. (6). Their work utilized metal extraction followed by reaction with phenylmagnesium bromide to form the phenylated metal species. Gas chromatographic separation with flame ionization detection was used.

The work to be described here involves the extraction of lead into chloroform, the evaporation of the solvent, and the methylation of the residue to generate tetramethyllead. The volatile analyte is then collected on a short trapping column prior to subsequent detection via atomic absorption spectrometry.

Lead was selected as a reasonable candidate for study in this extraction/methylation approach. Although lead has been converted to the hydride PbH<sub>4</sub>, somewhat specialized reaction conditions were required (7-9). A major reason for the choice of lead is the fact that well-developed methodologies exist for the determination of the methylated derivative,  $Pb(CH_3)_4$ . Used widely as an antiknock additive to gasoline, tetramethyllead has been determined in gasoline itself (10, 11), in the atmosphere (12-15), in water (16), and in biological samples (16). Although continuous detection systems have been utilized (17), the general approach involves low-temperature trapping of the lead alkyl compounds and/or a gas chromatographic separation. Of particular interest is an atmospheric trapping method described by Coker (18), and used in this work. It is reported that the analyte was retained at ambient temperature on a short column of Porapak Q, a porous polymer. Selective elution of various alkyllead species was then achieved by gradual heating of the column.

Atomic spectrometry lends itself well to the detection of volatile metal-containing compounds (19, 20). While flame atomic absorption spectrometry has been used as a detection system for organolead determinations, it is not as sensitive as absorption methods using furnace atomization (21) or as emission techniques utilizing microwave-induced plasmas for excitation (22, 23). The resistively heated quartz furnace described by Chau et al. (24) is appealing due to its low cost, ease of operation, selectivity, and sensitivity (subnanogram amounts of organolead compounds).

### EXPERIMENTAL SECTION

Apparatus. A Model 82-500 Jarrell-Ash atomic absorption spectrophotometer with a 100- $\mu$ m entrance slit and a 150- $\mu$ m exit