

THE USE OF LIQUID SCINTILLATION COUNTING IN THE  
STUDIES OF COAL AND COAL DERIVED LIQUIDS

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*Coal and coal derived liquids were treated with radio labeled ( $^{14}\text{C}$  or  $^3\text{H}$ ) acetic acid, ethanol, methanol and water. Coal derived liquids were allowed to react with 1- $^{14}\text{C}$ -acetic anhydride in pyridine to form acetate derivatives of phenols, alcohols, primary and secondary amines. The samples were then oxidized and collected  $^{14}\text{CO}_2$  or  $^3\text{H}_2\text{O}$  measured in a liquid scintillation counter. Good reproducibility and quantitative recovery of  $^{14}\text{CO}_2$  and  $^3\text{H}_2\text{O}$  were observed. The liquid scintillation counting method was very useful for quantitation of hydroxyl groups and primary and secondary amines in coal derived liquids. The amount of adsorption of acetic acid, ethanol, methanol, and water was also measured. They found it to be irreversibly adsorbed on coal. Other techniques, such as  $^1\text{H}$  and  $^{13}\text{C}$  nmr as well as titration of liberated acetic acid, are inefficient in quantitative determination of acid groups in coal. Only tracer methodology was able to determine adsorption of solvent on coal efficiently.*

## INTRODUCTION

Considerable effort in the past few years has been devoted to the development and the study of rapid and efficient analytical methods for the determination of functionality in coal and coal derived products (2-11). The determination of phenol and alcohol moieties by acetylation has been used routinely for several years (1,3-7). Recently several groups have used silylation in combination with infrared, (10) proton NMR (2) and atomic adsorption spectroscopy (3) to determine phenolic and alcoholic content of coal and coal derived products. Triethylborane activated by pivalic acid has been used very recently as a reagent for the determination of hydroxyl groups in lignites (11).

However, in most cases the reproducibility of results obtained often leaves much to be desired. Often it remains questionable whether or not the analytical reactions involved are quantitative. A rapid and efficient method for quantitation of phenols, alcohols, primary and secondary amines is to use a radio labeled acetic anhydride for acetylation of these moieties. Reacted coal samples could then be oxidized in an atmosphere of oxygen and carbon-14 and/or tritium thus converted to  $^{14}\text{CO}_2$  or  $^3\text{H}_2\text{O}$  could then be dissolved in a scintillator for counting in a liquid scintillation counter (12).

## EXPERIMENTAL

*Materials*

Solvent refined lignites (SRL) sample (M-11A) and two solvent refined coal (SRC) samples (AMAX, and Indiana) were ground to about 40 mesh for the study (13). Elemental analysis of the samples was performed by Spang Micro-Analytical Laboratory. 1- $^{14}\text{C}$ -Acetic anhydride (ca 10 Ci/ml) and 1- $^{14}\text{C}$ -acetic acid<sup>1</sup> (ca 10 Ci/ml) were used for radio labeled study. High-volatile bituminous coal, seam 6, from a West Central Illinois mine was ground to about 160-350 mesh for the study. Ethanol-1- $^{14}\text{C}$   $^3\text{H}_2\text{O}$  and methanol- $^{14}\text{C}$  (ca 5.5 Ci/ml) was used as solvent.

<sup>1</sup>Amersham/Searle, Arlington Heights, Illinois  
The New England Nuclear Corp., Boston, Massachusetts

*NMR Spectra*

Proton NMR spectra were measured on a Varian EM 390 nmr spectrometer. Samples were dissolved in pyridine-d<sub>5</sub> containing a calibrated amount of s-trioxane or octamethylcyclotetrasiloxane (OMTS) as standard. Correction for pyridine was based on a standard vs. residual pyridine integrated. Generally, seven integrations were run and averaged. Carbon 13 PFT-NMR were measured in a JOEL JNM-FX 60 spectrometer. Chloroform-d<sub>1</sub> was used as the solvent with OMTS as an internal standard.

*Acetylation with 1-<sup>14</sup>C-Acetic Anhydride*

(i) SRL and SRC samples (250mg) were allowed to react at room temperature for 24 h with 0.25 ml 1-<sup>14</sup>C acetic anhydride (ca 10 Ci/ml) in 3 ml pyridine under argon. The mixture was added to 2 liter water and precipitated derivative filtered. The residue on the filter was washed with water until the effluent was free of acid. The acetylated sample was then freeze-dried with benzene and finally in vacuum at 80° in an abderhalden apparatus. (ii) Samples were also allowed to react with 1-<sup>14</sup>C-acetic anhydride at room temperature for 48 h; and at reflux temperature for 24 h and 48 h. (iii) 2-Naphthol and carbazole were acetylated in a similar condition at room temperature for 24 h with 1-<sup>14</sup>C acetic anhydride.

*Incubation of 1-<sup>14</sup>C-Acetylated Samples with Nonradio Active Acetic Acid*

Part of the 1-<sup>14</sup>C-acetylated SRL and SRC samples (100 mg) dissolved in 5 ml acetic acid-pyridine mixture (1:5). The mixture was stirred at room temperature and added to a liter of water. The residue was filtered, washed and freeze-dried with benzene. Finally, the sample was vacuum dried at 80° in an abderhalden apparatus. 2-Naphthol-1-<sup>14</sup>C-acetate and carbazole-1-<sup>14</sup>C-acetate were incubated with acetic acid in pyridine.

*Saponification and Distillation of 1-<sup>14</sup>C-Acetic Acid*

The saponification of dried 1-<sup>14</sup>C-acetylated SRL and SRC samples (200 mg) were carried out with 0.3 g potassium hydroxide in 20 ml water-pyridine (3:1) at reflux temperature

for 20 h. The mixture was then acidified (pH 3.0) with concentrated sulfuric acid. The liberated  $1-^{14}\text{C}$  acetic acid was collected by distillation. Radio activity was measured by counting an aliquate of sample in an Insta-Gel<sup>1</sup> in a liquid scintillation counter. Insta-Gel is a scintillation cocktail for aqueous and nonaqueous samples.

*Incubation of Bituminous Coal with  $^3\text{H}_2\text{O}$ , Ethanol- $1-^{14}\text{C}$  and Methanol- $^{14}\text{C}$  and Subsequent Soxlet Extraction*

Bituminous coal (1.0g) was mixed with 10 ml solvent ( $^3\text{H}_2\text{O}$ , Ethanol- $1-^{14}\text{C}$  or Methanol- $^{14}\text{C}$ ) at room temperature and mixture was stirred for 24 h. The residue was filtered, washed and dried in vacuum at  $110^\circ$ . Part of the sample was transferred into a porcelain thimble and continuously extracted with ( $\text{H}_2\text{O}$ , Ethanol, and MeOH) in soxlet apparatus. The residue was then dried in vacuum at  $100^\circ$ .

*Liquid Scintillation Measurement*

All samples of  $1-^{14}\text{C}$ -acetylated SRL and SRC were weighed in combustocoones<sup>2</sup> and mixed with cellulose to insure a slow and uniform oxidation. The samples were then oxidized in a Packard Model 306 automatic sample oxidizer for subsequent liquid scintillation measurement of  $^{14}\text{CO}_2$ . Problems such as sample solubility and color quenching usually experienced in liquid scintillation counting were eliminated by this procedure. Chemical quenching is minimized and chemiluminescence is entirely eliminated. Because of this counting efficiency is increased and quench correction is unnecessary. For carbon-14 the oxidizer can accommodate a sample size equivalent up to 40 millimoles of  $\text{CO}_2$

The  $\text{CO}_2$  is dissolved by passing the combusted  $1-^{14}\text{C}$ -acetylated-SRL and SRC sample through a basic amine (Carbo-Sorb<sup>1</sup>). Carbo-Sorb is a high capacity  $\text{CO}_2$  absorber and 1 millimole absorbs 5.8 millimoles carbon dioxide at saturation.

The samples were absorbed in 9 ml of Carbo-Sorb and collected in low potassium glass scintillation vials.<sup>1</sup> To this were added 13 ml of homogeneous blend toluene based scintillator (Permafluor V<sup>1</sup>). Permafluor V contains 91% PPO (2,5 diphenyloxazole) as the primary scintillator and 9% POPOP (1,4-bis-2(5-phenyloxazolyl)-benzene) as the secondary scintillator.

<sup>1</sup>Packard Instrument Co., Downers Grove, Illinois

The samples were counted in a liquid scintillator spectrometer.<sup>2</sup> Quenching was monitored by employing automatic external standard ratio. The counting efficiency for carbon-14 was measured by using toluene-<sup>14</sup>C<sup>3</sup> as a reference standard. The efficiency factor was used to convert the collected data in counts per minute (cpm) to disintegration per minute (dpm).

To check whether complete oxidation was achieved or not we used carbazole-1-<sup>14</sup>C-acetate and 2-naphthol-1-<sup>14</sup>C-acetate as standard. The recovery of carbon dioxide in these cases were found to be 98±2%.

Generally, five runs were made on each sample. Each vial was counted for 10 minute cycles for a total of two cycles. Background was found to be approximately 30 cpm.

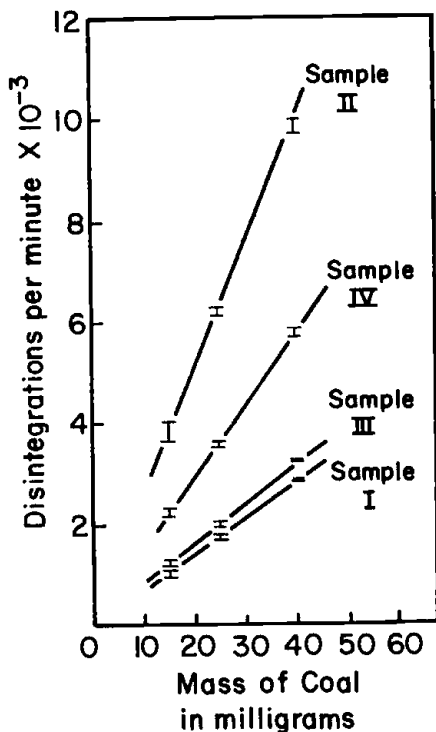


FIGURE 1. Recovery of <sup>14</sup>CO<sub>2</sub> in coal samples with increasing mass. Vertical bars represents twice the standard deviation.

<sup>2</sup>Model No. 3375, Packard Instrument Co., Downers Grove, Illinois

<sup>3</sup>The New England Nuclear Corp., Boston, Massachusetts

## RESULTS AND DISCUSSION

The results of our measurements of various coal samples are shown in Figure 1. The recovered carbon-14 activity in dpm is plotted against increasing mass of coal samples. The linearity of the plots reflects the efficient and quantitative recovery of  $^{14}\text{CO}_2$  in establishing the activity per unit mass for replicate samples.

Table 1 shows the results of radiolabeled study. Table 2 shows the chemical analysis of the SRL and SRC samples investigated. Since the model phenols and alcohols were acetylated quantitatively at room temperature, it was assumed that phenols and alcohols moieties in SRL and SRC will do the same. Primary and secondary amines were also reacted under this condition.

TABLE 1. Milliequivalent of Acetate per Gram of Sample in Various Reaction Condition

Sample	Reaction Conditions for $^{14}\text{C}$ -acetylation Time & Temp	Incubation conditions with ACOH/pyridine	Meq of acetate/g by $^{14}\text{C}$ study	Percent replacable hydrogen by $^{14}\text{C}$ study
<i>SRL</i>				
M11A	24h, r. t.	-	1.50	2.59
	24h, r. t.	24h, r. t.	1.39	2.40
	24h, reflux	-	2.92	5.03
<i>SRC</i>				
AMAX	24h, r. t.	-	1.88	3.41
	24h, r. t.	24h, r. t.	1.83	3.31
	48h, r. t.	-	1.90	3.44
	48h, r. t.	24h, r. t.	1.85	3.35
	24h, reflux	-	2.68	4.85
	48h, reflux	-	5.54	10.05
<i>Indiana</i>				
	24h, r. t.	-	2.17	3.49
	24h, r. t.	24h, r. t.	2.04	3.37
	48h, r. t.	-	2.20	3.61
	48h, r. t.	48h, r. t.	2.12	3.49
	24h, reflux	-	2.88	4.74
	48h, reflux	-	6.59	10.86

TABLE 2. Elemental Analysis of the SRL and SRC Samples (Wt%)

Sample	C	H	N	S	O	Ash
SRL						
M11A	89.31	5.80	1.11	0.86	2.35 <sup>a</sup>	<0.1
SRC						
AMAX	88.56	5.50	1.71	Trace	4.22 <sup>b</sup>	<0.1
Indiana	85.45	6.06	2.23	1.10	5.10 <sup>b</sup>	<0.1

<sup>a</sup> Measured by neutron activation analysis

<sup>b</sup> Measured by difference

Quantitative analysis of acetate groups in SRL and SRC samples were performed by a tracer study using <sup>14</sup>C-labeled acetic anhydride, proton nmr, carbon-13-nmr and saponification of acetate groups, followed by titration of liberated acetic acid. Comparison of results are reported in Table 3.

TABLE 3. Comparison of Results of Radio-Active Study Proton nmr, <sup>13</sup>C-nmr and Sapinification-Titration.

Sample	Reaction condition for <sup>14</sup> C-acetylation Time & Temp	Radio-Active Study	Percent Replacable Hydrogen		
			Proton nmr	<sup>13</sup> C-nmr	Saponification titration
SRL					
M11A	24h, r.t.	2.59	2.70 <sup>±</sup>	-	1.94
	24h, reflux	5.03	0.2	2.10 <sup>±</sup>	0.3
SRC					
AMAX	24h, r.t.	3.41	2.93	-	2.53
	48h, r.t.	3.44	3.08	-	-
	24h, reflux	4.85	4.23	3.70	4.21
	48h, reflux	10.05	5.50	-	-
Indiana					
	24h, r.t.	3.49	2.32	-	2.63
	48h, r.t.	3.61	2.41	-	-
	24h, reflux	4.74	3.53	-	3.90

Proton nmr measurements of the sample in pyridine-d<sub>5</sub> before and after acetylation were used to measure the fraction of acidic groups in the sample. In our study of several model compounds, the chemical shift of OH (phenols) and NH(carbazole) hydrogen in pyridine-d<sub>5</sub> are generally downfield (between 9.5 to 6.3 ppm, aromatic region) depending upon the concentration. Thus, prior to acetylation the acidic proton signals are located under the aromatic region. After acetylation the methyl group of the acetyl group signals are in the aliphatic region. The percentage H as acidic hydrogen can be then calculated from equation 1 where R<sub>1</sub> is the fraction of the aromatic proton (area) in acetylated samples and R<sub>2</sub> is the fraction of aromatic protons (area) in the nonacetylated samples. Absolute mole of hydrogen measurement of aliphatic area before and after acetylation of samples was also used to calculate percent acidic hydrogen.

$$\% \text{ H as acidic H} = \frac{R_2 - R_1}{2R_1 + 1} \times 10^2 \quad (1)$$

Measurement of percentage of acidic hydrogens by <sup>13</sup>C nmr was calculated from the relative area of the carbonyl carbon (169 ppm) to the total carbon atoms and from the carbon hydrogen elemental analysis (equation 2).

$$\% \text{ H as acidic H} = \frac{(\text{C=O area}) (\text{wt \% C}) (\text{wt \% H})^{-1} 10^2}{[\text{C}_{\text{total area}}^{-2} (\text{C=O area})]^{12}} \quad (2)$$

Carbon-14 measurements are described in the experimental. The disintegration per minute (dpm) per milligram of acetylated sample was converted to mmole of acetate per milligram of sample: (equation 3)

$$\frac{\text{mmol acetate}}{\text{mg acetylated sample}} = \frac{\text{dpm}(\text{mg acetylated})^{-1}}{\text{dpm}(2\text{mmol } 1\text{-}^{14}\text{C Ac}_2\text{O})^{-1}} \quad (3)$$

Following the correction of increase in weight due to the acetate groups (equation 4), percentage of acidic hydrogens was calculated. In general, carbon-14 techniques gave a 2% error with the model system 2-naphthyl-1-<sup>14</sup>C-acetate, and carbazole 1-<sup>14</sup>C-acetate.

$$\frac{\text{mmol acetate}}{\text{mg sample}} = \frac{\text{mmol acetate}(\text{mg acetylated sample})^{-1}}{1 - \frac{\text{mmol acetate}}{\text{mg acetylated sample}} \times 10^{-3} \times 42\text{mg}(\text{mmol})^{-1}} \quad (4)$$

Proton nmr, carbon-13 nmr and saponification titration gave a different number than carbon-14 study. Possibly, the adsorption of the acidic protons in proton nmr do not lie only under aromatic regions, as in model compounds, hence the percentage of acidic hydrogen by proton nmr will be less than expected. Alternatively, the carbon-13 nmr integrating data are also lower in values than that of radio labeled study. Which in turn means the precision is poorer. There is a small percentage of carbonyl carbon relative to total number of carbons and the difficulty in properly phasing the baseline in the C=O region of carbon 13 nmr. Saponification of acetate groups and then distillation of liberated acetic acid is a routine method for the determination of acetate groups. In our study, however, saponification followed by distillation of 1-<sup>14</sup>C-acetic acid always gave much less acetic acid than expected.

Radio labeled studies also showed that highertemperatures cause C-acylation of aromatics to occur. When the saponified residue, after distillation of 1-<sup>14</sup>C acetic acid followed by washing with water and freeze-drying with benzene, was measured for radio activity, it had almost 0.5 meq of acetate per gram of sample.

Additionally, almost 10% of acetate was found as adsorbed acetic acid. The incubation of radio-labeled sample with non-radio active acetic acid in pyridine caused a 10% decrease in the amount of acetate groups. The exchange of O-1-<sup>14</sup>C-acetate or N-1-<sup>14</sup>C-acetate with acetic acid was ruled out since 2-naphthyl-1-<sup>14</sup>C-acetate and carbazole-1-<sup>14</sup>C-acetate had the same specific activity after incubation with non-radio active acetic acid in pyridine.

We also found that water, methanol and ethanol adsorbed on coal. When high-volatile bituminous coal was treated with <sup>3</sup>H<sub>2</sub>O, methanol-<sup>14</sup>C, and ethanol-1-<sup>14</sup>C at room temperature for a period of 24h, the residue retained some radioactivity. The soxlet extraction with non-radio active solvent of these treated samples caused some decrease in the radio-activity. The results of this study are reported in Table 4.

TABLE 4. Adsorption of Solvent in Bituminous Coal

<i>Solvent</i>	<i>Reaction Conditions</i>	<i>mmole of solvent/ g of sample</i>
$^3\text{H}_2\text{O}$	(i) incubation for 24h at r.t.	0.24 mmole/g
	(ii) incubation for 24h, at r.t. and soxlet extraction with $\text{H}_2\text{O}$ for 24h.	0.18
$^{14}\text{CH}_3\text{OH}$	(i) incubation for 24h at r.t.	0.80
	(ii) incubation for 24h at r.t. and soxlet extraction with $\text{CH}_3\text{OH}$ for 24h.	0.56
$^{1-14}\text{C}-\text{C}_2\text{H}_5\text{OH}^{(a)}$	(i) incubation for 24h at r.t.	0.15
	(ii) incubation for 24h at r.t. and soxlet extraction with $\text{C}_2\text{H}_5\text{OH}$ for 24h.	0.08

(a) pre incubated coal with  $\text{C}_2\text{H}_5\text{OH}$  gave same results.

## CONCLUSION

The quantitation of hydroxyl groups by acetylation using tracer study is more reliable and efficient than  $^1\text{H}$  and  $^{13}\text{C}$  NMR techniques. Only tracer methodology was able to determine adsorption of solvent on coal efficiently.

## ACKNOWLEDGMENT

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13. The samples were obtained as follows: M11A (deashed) prepared by the University of North Dakota Chemical Engineering Department under Project Lignite, from North Dakota lignite. Conditions: 2500 psi of 1:1 CO<sub>2</sub>: H<sub>2</sub> at 479°C (max). AMAX Catalytic Inc., Wilsonville, Alabama from AMAX subbituminous coal from Bel Ayr Mine, Wyoming. Conditions: 2400 psi H<sub>2</sub> and recycle gases at 457°C (max) using recycle solvent heavy in phenols and 1,2 and 3 ring aromatics. Indiana, Catalytic Inc. Condition: 1700 psi H<sub>2</sub> and recycle gases at 441°C (max) using recycle solvent.