

A NEW DETERMINATION OF EXCHANGEABLE OXYGEN IN COALS

Edwin S. Olson and John W. Diehl

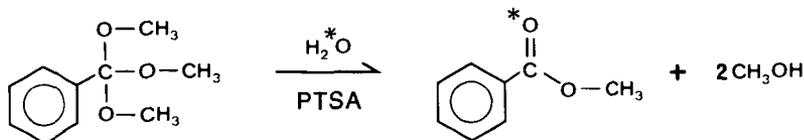
University of North Dakota Energy and Mineral Research Center
Box 8213, University Station
Grand Forks, ND 58202

Introduction

All facets of research on a coal sample require accurate knowledge of the moisture content, which obviously changes during any chemical or physical processing. The elemental analysis of coal significantly depends on the determination of the moisture content of the coal; and thus during the combustion (ultimate) analysis of a sample, the amount of water initially present in the coal sample must be accounted for in the water of combustion measured in the experiment, in order to determine the amount of hydrogen present in the coal sample. The amount of water present also must be known to determine the oxygen content. Although the weight loss drying method is standard practice for determining moisture, there are errors possible, especially in the low-rank coals, which may contain over 30 percent moisture. These errors could be due to incomplete drying or possibly oxidation during the determination.

Finseth has recently reported a new method for the determination of water in coals which utilizes isotope dilution (1). In this technique, a known amount of water which was enriched in ^{18}O was added to the weighed coal sample in a tube. Carbon dioxide was also added and the tube sealed and then heated to equilibrate the added labeled water with the natural abundance water present in the sample. The tube was then opened and the carbon dioxide analyzed by mass spectrometry to determine the isotopic ratio, from which the coal moisture could be calculated. The carbon dioxide acted as a probe molecule to facilitate the mass spectrometric analysis, since its oxygens exchange completely with those of the water. The results of Finseth's moisture determinations were compared with ASTM values for a number of Argonne premium coal samples and were in all cases somewhat larger than the ASTM values.

The mass spectrometers available in our laboratories are not adaptable to analysis of the CO_2 , hence we sought an alternative for the analysis of the isotope ratio in the isotopically equilibrated water samples. The reaction of the water with several orthoesters to give the ester containing the water-derived oxygen (labeled oxygen) in the carbonyl group was investigated (see Equation 1). The orthoester selected for the analysis was trimethyl orthobenzoate, since it gave methyl benzoate which could be conveniently analyzed in our GC/FTIR/MS system.



Equation 1. Reaction of trimethyl orthobenzoate with water.

Results and Discussion

The reaction of water with the trimethyl orthobenzoate proceeded somewhat slowly; hence several catalysts for the reaction were investigated. Boron trifluoride etherate was unsuccessful since it appeared to catalyze the exchange of labeled oxygen of the water with the glass or possibly with the solvent. Methanesulfonic acid similarly gave poor results. A very dilute solution of p-toluenesulfonic acid in glyme was selected as the catalyst which gave the best reproducibility and calibration.

The isotope ratio of the natural and labeled methyl benzoate which results from the reaction of water with the trimethyl orthobenzoate was determined both from mass spectra and infrared spectra of the methyl benzoate peak eluting from the GC column. Adequate peak shape was obtained using a 60 m x 0.32 mm column with a 1.0 μ DB-5 film, so that reproducible integration of the peak for the quantitation could be obtained.

In the mass spectral measurement, the ratio of the integrated intensity of the (M-31)⁺ ion corresponding to the labeled methyl benzoate (at m/e = 107) to that of the natural methyl benzoate (at m/e = 105) over the corresponding peaks was determined. A representative mass spectrum from the GC/MS determination of one of the known mixtures is shown in Figure 1 along with the reconstructed total ion chromatogram which shows the ¹⁸O-labeled and natural methyl benzoate peak and the unreacted trimethyl orthobenzoate peak.

A linear calibration plot (Fig. 2) was used for the mass spectral isotope ratios, since there were no overlapping peaks from the labeled compound (m/e = 107) and natural abundance analyte (m/e = 105). The small amount of m/e 105 peak in the spectrum of the labeled ester was due to the small amount of ¹⁶O water (2 percent) in the ¹⁸O water plus a small amount in the glyme solvent used in the reaction of the water with the orthoester. The glyme was purified and dried over lithium aluminum hydride and distilled onto molecular sieves. The m/e 105 peak in the standard will not affect the linearity but will change the intercept.

The absorbance reconstructed GC peaks of the natural methyl benzoate (over the range 1750 to 1742 cm⁻¹) and labeled methyl benzoate (over the range 1720 to 1712 cm⁻¹) were integrated to obtain the area ratios (A/S) of natural to labeled ester. A representative infrared spectrum from the GC/FTIR determination of one of the known mixtures is shown in Figure 3.

The calibration plot (Fig. 4) of the infrared data (amount ratio versus area ratio) was not linear since the absorption bands for the labeled and natural ester overlap slightly. The calibration data were fitted to a polynomial expression, which was then used for the determination of the unknown isotope ratios.

Three methods were investigated for the equilibration of the coal moisture with the added isotopically enriched standard. The equilibration was first carried out by adding a solution of the ¹⁸O water in dried and purified glyme to the coal and heating in the sealed vial at 100°C overnight. Decent calibration curves were obtained by using volumetric aliquots of known concentrations of natural abundance and isotopically enriched water in glyme. The area ratios were reproducible, with deviations less than one percent for most points. Tests of the calibration with known concentrations of water in glyme showed that the method was accurate. However, tests with coal samples gave obviously poor results using this method. Exchange with the ether oxygen of the solvent appears to have occurred in the coal determinations, rendering the method useless. The same reaction in the absence of the coal but with an amount of natural abundance water corresponding to that expected in the coal gave no exchange with the solvent, even in the presence of acid catalyst. Acetonitrile was investigated as the solvent, but the methyl benzoate did not form.

The equilibration was then investigated using no solvent as Finseth has reported. To generate the calibration curves, the ¹⁸O water and natural abundance

water were pipetted into a vial using micropipettes. Trimethyl orthobenzoate and catalyst were added and the vial was crimped. The methyl benzoate product was analyzed with GC/FTIR/MS as described above. The resulting calibration curves were somewhat erratic, and although points from the same solution were reproducible, tests of the calibration with new known mixtures gave large errors. The large errors and erratic calibration curves were attributed to errors in the volumetric measurements using the micropipettes, probably due to incomplete drainage.

Finally, the solutions for the calibration were made up by weighing milligram amounts of ^{18}O water and natural water. A linear calibration curve was obtained from the mass spectral data, and a smooth curve was obtained from the infrared data, from which a polynomial expression was derived. The infrared integrated absorbance ratios were reproducible within one percent, and the mass spectral intensity ratios were within one percent in the middle of the calibration curve and within four percent at each end. A test of the calibration using a new known solution gave errors of 1.8 percent using the infrared data and 4.5 percent using the mass spectral data.

The method was tested using a Beulah lignite sample by adding an analytically weighed amount of the ^{18}O water. The sample was sealed with a torch in such a manner as to leave a capillary at the sealed end. After equilibration in an oven overnight, the sample was then removed from the oven and placed in an oil bath so that the coal in the bottom of the tube was warmed and the moisture collected in the capillary tube. The tube was opened and the equilibrated water was obtained from the capillary and reacted with trimethyl orthobenzoate and p-toluenesulfonic acid catalyst. The analysis of the methyl benzoate with the GC/FTIR/MS system gave values for the exchangeable oxygen reservoir of 39.8 percent from the infrared data and 38.6 percent from the mass spectral data. The close agreement of these determinations was encouraging and demonstrated that the instrumental methodology was working extremely well. On the other hand, the large value obtained was not expected, since the ASTM drying weight loss method gave 33.6 percent moisture in this sample. The equilibration with the isotopically enriched water, of course, determines the size of the exchangeable oxygen reservoir. The problem is that we do not know if this includes portions of the organically bound oxygen, such as carboxylic acid groups. Finseth demonstrated that benzoic acid does not exchange under these conditions, however, we cannot be certain that the coal carboxylate and carboxylic acid groups do not exchange, considering that there may be catalysts for the exchange present in the coal.

The exchangeable oxygen determination was then performed on two of the Argonne premium coal samples and a sample of Big Brown lignite. Table 1 compares the values obtained using the isotope dilution GC/FTIR and GC/MS data with the fast drying ASTM method and the Finseth isotope dilution (CO_2) MS method. The values obtained for the Argonne premium sample of Illinois #6 bituminous coal and the Argonne premium Beulah-Zap lignite were very similar to those obtained by Finseth (1) and were somewhat higher than those found using the ASTM method. Further work with the Argonne premium samples will be undertaken to evaluate the infrared and mass spectral methods for water determination.

Experimental

Coal samples were equilibrated with the weighed amount of ^{18}O water in sealed tubes at 100°C for 15 hours as reported by Finseth (1). The seal on the tubes was fashioned so that it formed a narrow capillary portion. After equilibration, the bottom of the tube was warmed so that moisture was trapped in the capillary portion of the tube. The capillary tube was then broken off, and the upper part containing the collected water was quickly transferred to a reaction vial, where it was crushed and the reagents added. For preparation of the derivative, $1\ \mu$ of a solution containing $1\ \text{mg/ml}$ of p-toluene-sulfonic acid in dried glyme and $100\ \text{mg}$ of trimethyl orthobenzoate were added to the vial, which was sealed with a crimped cap. The vial was heated for 1 hour at 100°C . Instrumentation for the GC/FTIR/MS determination was described earlier (2). All glassware was dried several hours at 110° .

References

1. Finseth, D. ACS Div. of Fuel Chem. Preprints, (1987) 32(4), 260-5.
2. Olson, E.S. and Diehl, J.W., Anal. Chem. (1987) 59, 443.

Acknowledgements

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TABLE 1. MOISTURE (EXCHANGEABLE OXYGEN) DETERMINATIONS

<u>COAL</u>	<u>ID/GC/FTIR</u>	<u>GC/MS</u>	<u>ID/MS(CO₂)[*]</u>	<u>ASTM</u>
AR. B-Z LIGNITE	34.3%	32.8%	34.4%	32.8%
AR. ILL #6	9.4%	9.9%	9.6%	8.8%
UND B-Z LIGNITE	39.8%	38.6%		33.6%
UND BB LIGNITE	28.9%	29.4%		27.8%

• Values from Finseth (Reference 1)

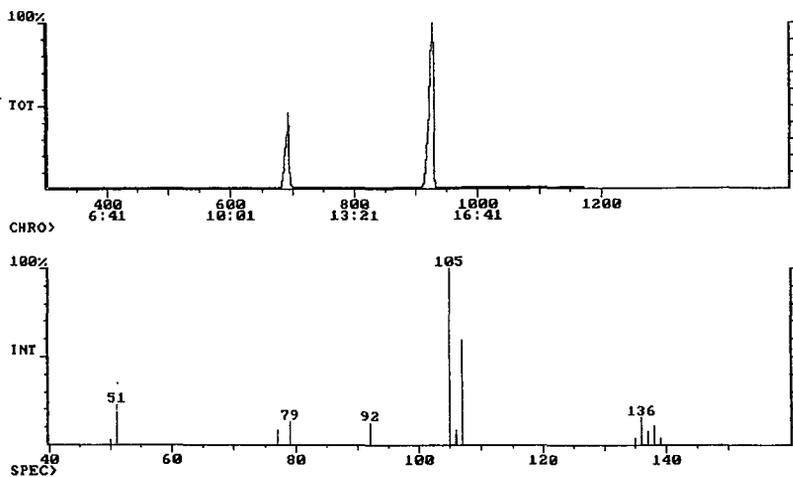


Figure 1. (a) Reconstructed total ion chromatogram of mixture of ^{18}O - and ^{16}O -labeled methyl benzoate, (b) Mass spectrum of above mixture.

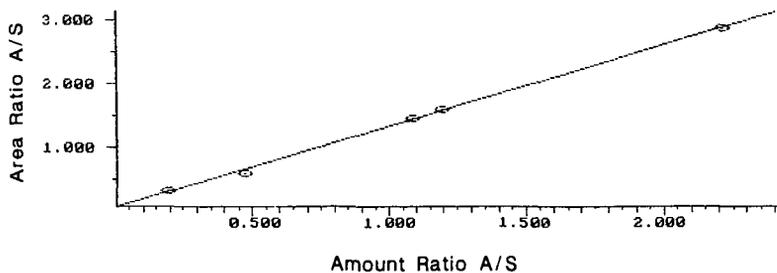


Figure 2. Mass spectra calibration curve for isotopic methyl benzoate ratios.

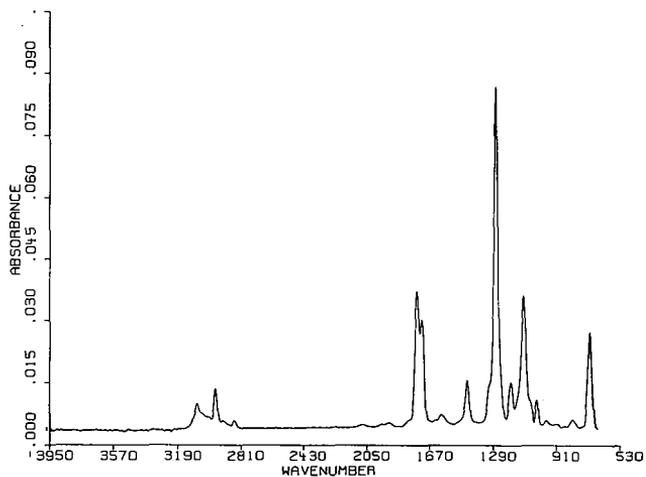


Figure 3. Infrared spectrum of mixture of ¹⁸O and ¹⁶O-labeled methyl benzoate.

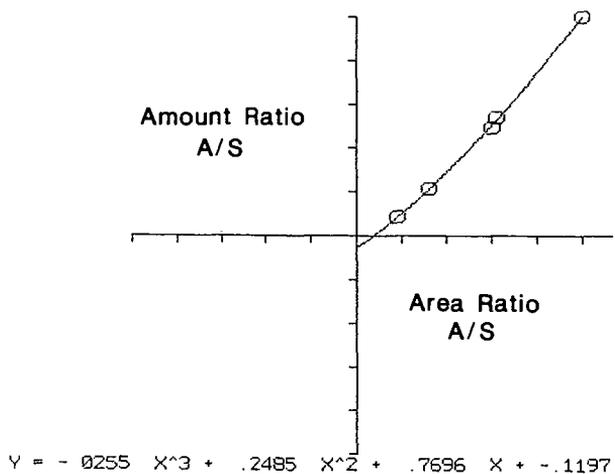


Figure 4. Infrared calibration curve for isotopic methyl benzoate ratios.