

## RAPID DETERMINATION OF NITROGEN IN COAL

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### ABSTRACT

A simple and rapid colorimetric method for the determination of total nitrogen in coal has been developed. The method is based on the rapid digestion of the coal sample with a mixture of 50% hydrogen peroxide plus concentrated sulfuric acid and subsequent color development with Nessler's reagent for the determination of ammonium nitrogen. In this procedure, 250 mg of finely ground coal are digested within 30 minutes by heating with 25-60 ml of a 4:1 mixture of  $H_2O_2$  -  $H_2SO_4$  in a special Digesdahl® apparatus. After boiling to destroy excess hydrogen peroxide and cooling, subsequent color development and spectrophotometric measurement at 460 nm take only about 5 minutes. Application of this procedure gave good results for the nitrogen values of two NBS coal samples and reasonably good agreement for Illinois and Iowa (run-of-mine and physically and chemically cleaned) coal samples analyzed by a modified Kjeldahl procedure.

### INTRODUCTION

The determination of total nitrogen in coal is usually performed by ASTM Method D-3719 (1) or by using commercial C, H, N, analyzers. The former procedures are based on the time-honored Kjeldahl method, involving long digestion times, difficult distillations, and tedious titration finishes. The fact that the literature is extensive (2) on various modifications of the Kjeldahl method for nitrogen in coal points to the inadequacies which plague this difficult but necessary procedure. The instrumental methods, on the other hand, require fairly expensive apparatus and may suffer in accuracy because the very small sample sizes combusted could be not too representative of the entire batch.

Recently, the determination of organic nitrogen has been simplified by a rapid and reliable procedure for digesting agricultural samples (3). The digestion is readily accomplished in a simple apparatus by the powerful mixture of hydrogen peroxide and sulfuric acid, and the final measurement is made spectrophotometrically using Nessler's reagent. Most of the necessary digestion parameters have been already established in that work.

The utility of this simple apparatus has been also demonstrated on the rapid digestion of coal samples by a mixture of nitric, phosphoric, and perchloric acids for the subsequent determination of sulfur and iron in coal (4). Because of the success of this method on agricultural samples and because of the ease of using the digestion apparatus, this work was undertaken to apply it to the determination of total nitrogen in coal.

## EXPERIMENTAL

### Coal Samples

The three coals in sample series 101-304 were high volatile C bituminous coals. The ROM Illinois No. 6 coal came from the Elm Mine, near Trivoli, Illinois. The Iowa coal in the series 201-204 was freshly mined near Lovilia, Monroe County, Iowa, and subsequently cleaned at the Iowa State University coal preparation research facility, using a heavy-media (magnetite) process at 1.3 sp. gr. The ROM coal in the series 301-304 came from the same region in Iowa but it was stored in the laboratory for a prolonged period; thus it was probably heavily oxidized. The chemical desulfurization treatment consisted of leaching with hot  $\text{Na}_2\text{CO}_3$  solutions containing oxygen under pressure. Subsequent extractions were conducted with boiling 1:7  $\text{HNO}_3$  for 30 minutes. Further description of these samples and chemical treatments is provided elsewhere (5).

Sample No. 500 was an Upper Freeport coal provided by the Massey Coal Co., Inez, Kentucky. The NBS samples were obtained from the National Bureau of Standards.

### Apparatus

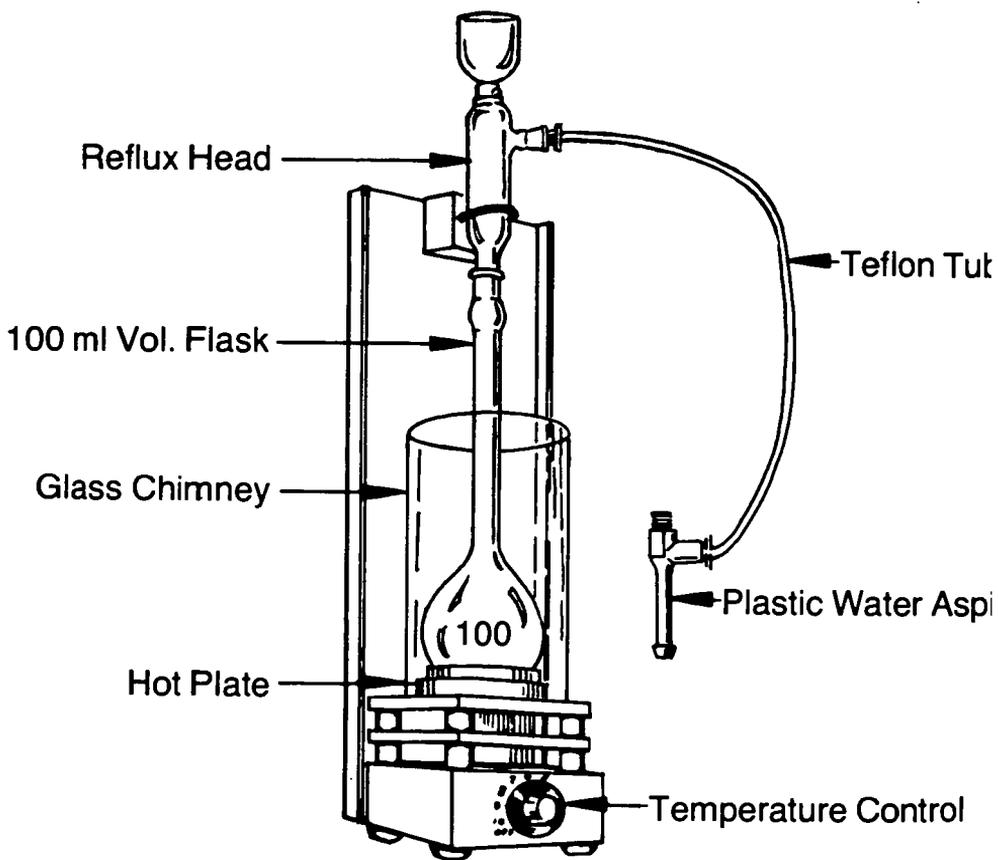
The samples were digested in a Hach Model 21400 Digesdahl® apparatus consisting of a heating unit, a 100-ml volumetric flask, surrounded by a glass chimney to diminish heat loss and thus reduce the digestion time, and a reflux head manifold at the top of the flask, connected via a Teflon tube to a plastic water aspirator to remove fumes. This simple and inexpensive apparatus is depicted in Fig. 1. The 25-to-250 watt disc-element heater is supplied with a solid-state controller. The colorimetric measurements were made at 460 nm with a Hach Model DR/2 single-beam spectrophotometer using a 2.5-cm flow-through cell.

### Reagents

The digestion mixture was premixed using 4 parts of 50% hydrogen peroxide and 1 part concentrated sulfuric acid. CAUTION: This reagent is a powerful oxidizer and should be handled very carefully. However, it is stable during prolonged storage. The Nessler's reagent and the polyvinyl alcohol (as a 0.1 g PVA solution per liter) were obtained from the Hach Company.

### Digestion Procedure

A weighed sample (~250 mg) of finely ground coal (60 mesh) is placed in the 100-ml volumetric flask. (As a convenience, the sample can be weighed onto a piece of plastic kitchen wrap which is then folded up and pushed down the neck of the flask). About 4-5 ml of concentrated  $\text{H}_2\text{SO}_4$  is added to the flask, the flask is placed on the heater, and the reflux head manifold is attached to the top of the flask and connected to a water aspirator. The mixture is digested for ~5 min. at a medium-to- high setting to carbonize the sample, until the  $\text{H}_2\text{SO}_4$  solution refluxes to the top of the head. The flask is then removed from heat, allowed to cool for ~2 min., and ~20 ml of the 4:1  $\text{H}_2\text{O}_2$ - $\text{H}_2\text{SO}_4$  digestion reagent is cautiously added through the side arm funnel of the manifold. (If the addition is too fast, some spattering may occur.) The flask is returned to the heater for further digestion. After ~5 min., more of the reagent can be added through the side arm and boiling is continued until the solution is fairly clear. Additional boiling for ~5 min. is then required to remove excess  $\text{H}_2\text{O}_2$ , until refluxing of  $\text{H}_2\text{SO}_4$  is observed. The



### DIGESDAHL DIGESTER

Fig. 1. Digesdahl apparatus for rapid digestion of coal samples.

digested sample is then removed from the heater, cooled, and diluted to the 100-ml mark with deionized water.

#### Spectrophotometric Measurements

A 0.5-ml aliquot of the diluted digestate is pipetted into a 25-ml mixing cylinder and diluted to mark with the 0.1 g/L PVA solution. Then 1.0 ml of Nessler's reagent is added, and the cylinder is stoppered and inverted several times to mix the contents. The mixture is poured immediately into the flow-through cell of the spectrophotometer that has been zeroed and standardized with the 0.1 g/L PVA solution at 460 nm, and the % transmittance is read to determine the nitrogen level from a standard calibration curve.

#### Calibration Procedure

The calibration standards can be conveniently prepared using Voluette Ampule Standards for ammonium nitrogen (160 mg N/L) in the amounts of 0.01, 0.2, 0.3, and 0.4 ml. To each, 0.5 ml of a blank digest is added and dilution to 25.0 ml is made with the PVA solution. After addition of 1.0 ml of Nessler's reagent to each mixing cylinder, the % transmittance is measured as above. The standards represent 0, 0.64, 1.28, 1.92, and 2.56 mg of N/L which corresponds to 0, 1.28, 2.56, 3.84, and 5.12% N in coal, respectively.

### RESULTS AND DISCUSSIONS

The percent nitrogen values determined by this new method for various coal samples are presented in Table 1. In most cases, there is reasonable agreement between these values and conventionally determined values. Except for samples 101 and NBS 1635, the nitrogen values obtained by this method are slightly lower in every other case. This "apparent loss" needs to be studied further in order to decide which method is subject to a possible systematic error. The precision of our method, as illustrated by the results in Table 2, appears to be good. But there may be sources of error which could be eliminated or minimized in order to bring our results in closer agreement with conventional results.

Of course, the coal samples in series 101-304 are very unusual in that they have been chemically treated and probably nitrated during the extraction with nitric acid. The effect of such chemical alteration of coal samples on the determination of nitrogen by this method needs to be examined.

### CONCLUSIONS

The simple and rapid digestion of organic samples with a 4:1 mixture of  $H_2O_2-H_2SO_4$ , previously developed for protein nitrogen in agricultural samples, has been adapted for the determination of total nitrogen in coal. The digestion is usually complete within 30 minutes, and the subsequent spectrophotometric measurement after Nesslerization requires about 5 minutes. The results of this method agree reasonably well with those of conventional methods. Although the precision is good, the absolute values are slightly lower than those obtained by Kjeldahl procedures, pointing to the necessity of further research to minimize this discrepancy. The clear digestate could be possibly used for additional analyses for such elements as phosphorus, calcium, magnesium, and other metals.

Table 1. Total nitrogen values in various coal samples, determined by conventional methods and by the new method described.

Sample No.	Coal Description	% Nitrogen Sample	
		Conventional <sup>a</sup>	New Method
101	Illinois No. 6 coal, ROM	0.82	0.90 <sup>b</sup>
102	#101 after chemical desulfurization	0.93	0.90
103	#101 after HNO <sub>3</sub> extraction	4.26	3.91
104	#102 after HNO <sub>3</sub> extraction	3.66	3.42
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201	Iowa coal (ISU precleaned)	1.31	1.20
202	#201 after chemical desulfurization	1.43	1.17
203	#201 after HNO <sub>3</sub> extraction	4.63	4.23
204	#202 after HNO <sub>3</sub> extraction	3.73	3.45
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301	Iowa coal, ROM	1.15	0.85
302	#301 after chemical desulfurization	1.17	0.84
303	#301 after HNO <sub>3</sub> extraction	3.74	3.55
304	#302 after HNO <sub>3</sub> extraction	3.43	2.99
500	Upper Freeport	1.30	1.27 <sup>c</sup>
NBS 1632a	Penn Seam Bituminous	1.27	1.26
NBS 1635	Colorado Subbituminous	1.0-1.3	1.38

<sup>a</sup> Conventional N values for the series 101-304 were provided by a modified Kjeldahl method in which 1.8 g of coal was digested with HgSO<sub>4</sub> catalyst at about 390-400°C. Sample 500 was analyzed by a commercial laboratory using an ASTM procedure. Values for the NBS coals were obtained from a literature compilation study (6).

<sup>b</sup> Average of triplicate determinations.

<sup>c</sup> Average of duplicate determinations.

Table 2. Reproducibility of nitrogen determinations by new method described.

Sample No.	Description	% Nitrogen	
		Replicate Detns.	Average
101	Same sample as in Table 1	(0.92, 0.89, 0.90)	0.90
500	Same sample as in Table 1	(1.23, 1.31)	1.27
NBS 1635	Different split, analyst, and time than in Table 1	(1.24, 1.26, 1.32)	1.28

#### ACKNOWLEDGMENTS

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