

## BASIC NITROGEN IN COALS

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### INTRODUCTION

The organic structure of a wide range of coals contains about 1.5 to 2.0 per cent of nitrogen, but little is known about the type of grouping in which this occurs.

Previous investigators found that extraction of a lignite with boiling dilute acid removed about twenty per cent of the nitrogen, mostly as amino acids (1), but only 5 per cent of the nitrogen of higher-rank coals could be identified by this method. Solvent extracts of a bituminous coal were found to be only slightly soluble in aqueous acid (2). Pyridine carboxylic acids are formed at an intermediate stage in the Kjeldahl nitrogen determination (3) and heterocyclic nitrogen compounds are present in distillation products of coals. Hence it has been assumed that much of the nitrogen is present in cyclic structures. However, heterocyclic nitrogen could not be detected by exhaustive methylation of a coal, even after hydrogenation (4).

The sorption of perchloric acid from an anhydrous perchloric-acetic acid mixture (5) has been used in these laboratories for the estimation of basic groups in pitch and tar fractions (6). The same reagent can be used for the detection of basic groups in coals, if the coal is first dissolved or dispersed in an acidic or neutral solvent. Phenol,  $\alpha$ -naphthol, and phenanthrene were found to be suitable for this purpose. The perchloric acid reacts with primary, secondary, and tertiary amine groups, including cyclic bases of the pyridine type, but the very weakly basic or acidic nitrogen structures of the thiazole, oxazole, pyrrole, indole, carbazole, or triazole types are not determined.

### EXPERIMENTAL

The ultimate analyses of the coals and vitrains examined are given in Table I. The finely ground coal (0.4 gram, minus 200 B.S. mesh) and phenol (10 grams) were gently boiled together under reflux for two hours under nitrogen, then cooled and washed into the titration vessel with 40 ml. of glacial acetic acid. 5 ml. of 0.2 N perchloric acid in glacial acetic acid was added and after 10 minutes the excess perchloric acid was titrated potentiometrically with pyridine (0.2 N) in glacial acetic acid, using a combined glass-calomel electrode. The basic nitrogen content of the coal was calculated from the amount of perchloric acid consumed.

It was established that none of the perchloric acid was consumed by oxidation of the coal: the same titration value was obtained with one coal after the perchloric acid had been replaced by sulphuric acid in acetic acid.

In the determination of total nitrogen the accuracy was  $\pm 1$  per cent of the total. A similar level was reached in the titrations, and the values of percentage basic nitrogen recorded in Fig. 1 are thus accurate to within about  $\pm$  two per cent for the bituminous coals.

## DISCUSSION AND CONCLUSIONS

Fig. 1 shows that for a wide range of coals about fifty to seventy per cent of the nitrogen is in a basic form. When the vitrain samples with carbon content 83.6 to 88.4 per cent were dispersed in phenol, or  $\alpha$ -naphthol, 57 to 62 per cent of the nitrogen was found to be basic, the percentage rising regularly with increasing carbon content. For vitrains containing more than 89 per cent carbon the basic nitrogen value appeared to be much lower. An interesting difference was noticed when the same set of vitrains was titrated after being dispersed in boiling phenanthrene. With increase in carbon content from 83.6 per cent to 88.4 per cent the nitrogen content was found to decrease regularly from 32 per cent to 21 per cent, but it then rose to a maximum of 54 per cent in a vitrain containing 89.5 per cent carbon. The basic-nitrogen values for this last sample and for the vitrains of still higher rank were greater when phenanthrene was used instead of phenol as the dispersing agent. This result doubtless reflects the greater solvent power of phenanthrene for high-rank coals. In  $\alpha$ -naphthol, high- and lower-rank bituminous coals gave almost the same values of basic nitrogen as in phenol.

The coals containing less than 80 per cent carbon were not petrographically homogeneous and showed a wider scatter of results than the vitrains. Even so, the proportion of the nitrogen in coals that is basic does not vary widely in a range from brown coal to high-rank coking coals.

Sharp end-points were obtained in the back titration of the excess perchloric acid except with the brown coals, for which originally very high values of basic nitrogen had been obtained, some being apparently greater than 100 per cent of the total nitrogen. This effect was thought to be due to the presence in the coal of inorganic ions ("humic" salts), since it is known (7) that metallic salts of carboxylic acids titrate as bases under the conditions of the experiments. The brown coals examined contained about two milli-equivalents per gram of carboxyl groups, partly neutralized as inorganic salts (8). After treatment of the brown and sub-bituminous coals with dilute aqueous acid, sharper end-points were obtained and the observed values of basic nitrogen were 50 to 73 per cent of the total.

The titration was not affected by the presence of carbonate minerals in some of the coals; such salts are not decomposed by the anhydrous acid used.

On an atomic basis, the total nitrogen groups vary from 0.7 per 100 carbon atoms in a brown coal to 1.7 per 100 carbon atoms in a high-rank coking vitrain. Over the same range, the variation in total oxygen groups is from 26 per 100 carbon atoms to 2.9 per 100 carbon atoms. In the low-rank coals nitrogen forms only a minor proportion of the functional groups, but in the high-rank coking coals oxygen- and nitrogen-containing groups are present in similar amounts. The two types of groups may affect the mode of thermal decomposition of the latter coals during carbonization to a similar extent.

The oxygen is more readily driven off from heated coal than is the nitrogen. With a coal containing about 89 per cent carbon, the variation of oxygen and nitrogen content (expressed on an atomic basis) with increasing temperature is as given in Table II.

The greater retention of nitrogen at higher temperatures is perhaps an indication that, unlike oxygen, it is present in cyclic structures in the original coal.

In conclusion, the present investigation has shown for the first time that a major proportion of the nitrogen in a wide range of coals occurs in the form of basic primary, secondary, and tertiary amine groups. These may occur in cyclic structures.

Efforts are now being made in these laboratories to determine the type of nitrogen-containing groups in carbonized coals.

#### ACKNOWLEDGEMENTS

The coals used and the analyses quoted were obtained in the course of the assessment of the coal resources of Australia which is being carried out under the direction of Mr. H.R. Brown, Chief, Division of Coal Research, C.S.I.R.O., to whom the authors are indebted for his support and for his advice on the preparation of this paper for publication.

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TABLE I

ULTIMATE ANALYSIS AND BASIC NITROGEN CONTENTS OF COALS (PER CENT, D.A.F.)

Coal	Carbon	Hydrogen	Nitrogen	Basic N <sub>2</sub>	Basic N <sub>2</sub> Total N <sub>2</sub> (%)	Solvent
Dawson Valley	91.4	4.4	1.9	0.09	5	Phenol
				0.61	32	Phenanthrene
Kemmis Creek*	90.3	5.1	1.6	0.13	8	Phenol
				0.58	36	Phenanthrene
Bulli*	89.5	5.3	1.8	0.47	26	Phenol
				0.98	54	Phenanthrene
Bulli*	88.8	5.4	1.5	0.88	58	Phenol
Tongarra*	88.4	5.4	1.7	0.98	57	Phenol
				1.06	62	α-Naphthol
				0.36	21	Phenanthrene
Bulli	87.7	5.0	1.6	0.76	48	Phenol
Tongarra*	87.4	5.4	1.6	0.99	61	Phenol
				0.32	20	Phenanthrene
Wongawilli*	85.3	5.4	1.9	1.12	60	Phenol
				0.55	30	Phenanthrene
Borehole*	84.4	5.7	2.2	1.29	59	Phenol
Borehole*	83.6	5.4	2.1	1.19	57	Phenol
				1.15	55	α-Naphthol
				0.68	32	Phenanthrene
Callide	79.9	4.4	1.3	0.88	69	Phenol
Collie	79.9	4.1	1.5	0.74	50	Phenol
Callide	78.7	4.2	1.2	0.87	74	Phenol
Ravensworth	78.4	4.8	1.9	1.13	59	Phenol
Muja	75.2	4.2	1.1	0.75	59	Phenol
Collie	74.3	5.0	1.3	0.69	52	Phenol
Morwell	70.3	4.9	0.7	0.43	63	Phenol
Yallourn	67.9	4.6	0.6	0.43	70	Phenol

\* Vitrain

TABLE II

Coal	N Atoms/100 C Atoms	O Atoms/100 C Atoms
Coal	1.5	3.3
500°C. coke	2.0	2.5
700°C. coke	1.8	1.7
900°C. coke	1.5	0.4

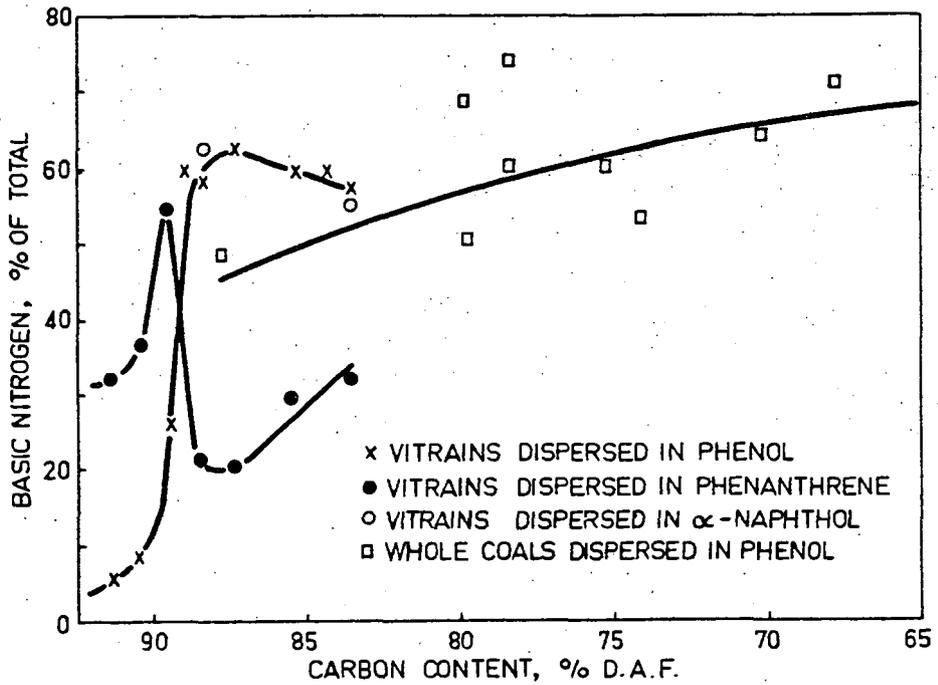


FIG.1.- PROPORTION OF NITROGEN IN BASIC FORM IN COALS