

## VERIFICATION OF THE AIDA'S CHEMICAL DETERMINATION METHOD FOR OXYGEN-FUNCTIONALITY IN COAL AND COAL PRODUCT

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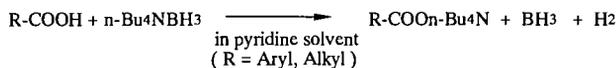
### INTRODUCTION

Coal contains various type of chemical functionality. It is believed that the oxygen-containing functionality in coal plays very important role to control its physical and chemical properties. Particularly, since a carboxylic acid and phenolic hydroxyl functionality have a relatively strong acidic characteristic comparing with other functionality such as alcoholic hydroxyl functionality, they can induce strong cohesive forces like a hydrogen bonding, which seems to be responsible to determine many characteristics of coal based on the macromolecular network structure. Thus, it is critical to have the quantitative information about such functionality as carboxylic acid and phenolic hydroxyl functionality in coal or coal product in order to develop the efficient chemical transformation processes of coal such as a liquisfaction, gasification, chemical desulfurization, etc..

It has long been a common sense in the coal science community that the hydrogen bonding contribution by carboxylic acid functionality to the chemical and physical property of coal could be almost negligible toward the high ranked coals like a bituminous coal, simply because of the very small amount of the functionality, which used to be determined by the chemical method developed by Blom et al.[1] about 40 years ago.

Although the recent development of sophisticated instrumentation such as FT-IR, <sup>13</sup>C-NMR, XPS, etc., has made it possible to provide quite reliable information about such hetero-atom-functionality as sulfur-, nitrogen- and oxygen-containing functionality, they still seem to fall into a common problem, that is, the low accuracy to determine a small amount of the functionality.

Recently, we had developed a chemical method [2], using following chemical reactions.



This method has several advantages compared to the conventional one mentioned above.

First of all, this reaction proceeds quantitatively with a single step in pyridine solution generating a gaseous product, H<sub>2</sub>, which, gives us much better accessibility of the chemical reagent to the carboxylic acid functionality buried into macromolecular network structure of coal than in aqueous solution reaction(cf. Blom's method) based on the swelling behavior, and also a reasonable accuracy due to the volumetric determination of the gaseous product (H<sub>2</sub>).

Secondly, this reaction exhibits a significant difference of the reaction rate depending upon the acidity of functionality, which makes easy to distinguish other functional groups such as phenolic and alcoholic hydroxyl functionality by using more reactive chemical reagents. Figure 1 demonstrates one of the examples of our experiment [3], which were carried out by using n-Bu<sub>4</sub>NBH<sub>4</sub>, LiBH<sub>4</sub> and LiAlH<sub>4</sub> as reactants, and determined the distribution of oxygen functionality in the pyridine extract of coal. Although we have not enough data concerning the difference of functionality between coal and pyridine extract at present moment, 8.0fold difference between our data and previous one [4] seems to be too much and quite interesting.

Most striking experimental result came out from the -COOH determination for various kind of coals, as shown in Figure 2, which demonstrates the coal rank dependency of the -COOH content, comparing the data previously reported[5]. Very interestingly, there is a quite large discrepancy in the range of high rank coal. This fact convinced us that our approach to develop more reliable chemical determination method could be right, because the coal swelling in water used to be dramatically decreased over higher rank region than sub-bituminous coal.

As Niksa pointed out in his recent personal communication and paper [6], it was well-known contradiction that the most of the CO<sub>2</sub> released during the pyrolysis of sub-

bituminous and bituminous coals could not be rationalized with the uni-molecular decomposition chemistry of carboxylic acid functionality in coals. Because the amount of carboxylic acid functionality reported in the raw coal was too small to handle it.

In order to verify the analytical data obtained by our new methodology, we have conducted a non-aqueous titration as an alternative method. In this paper, we like to report the experimental results

## EXPERIMENTAL

The chemical reagents were commercial products (Aldrich's gold label grade) which were used without further purification. Pyridine for the chemical determination of carboxylic acid functionality was dried over calcium hydride and distilled before use.

Coals from the Argonne National Laboratory (premium) and the Ames Coal Library were ground, seized, and dried with a silica-gel at room temperature under vacuum for three days, and stored under a dry nitrogen atmosphere. The pyridine extract of coal was prepared by means of the ultrasonic irradiation method [7].

A typical procedure of the non-aqueous titration of carboxylic acid and phenolic hydroxyl functionality in coal extract was as follows: 100mg of coal extract was dissolved in 5.0ml of dried pyridine, and placed into a Pyrex cell under N<sub>2</sub>-atmosphere which has an Pt-electrode and magnetic stirrer. The solution was potentiometrically titrated with a pyridine solution of n-Bu<sub>4</sub>NOH (0.1mol/l).

## RESULTS AND DISCUSSION

### 1. Non-aqueous titration of model compounds

Benzoic acid and 2-naphthol were used as model compounds for carboxylic acid and phenolic hydroxyl functionality, respectively. The non-aqueous titration of each functionality was carried out in pyridine solution by using n-Bu<sub>4</sub>NOH (0.1mol/l) pyridine solution as a titrant. The reaction is considered to proceed with following chemical equations.

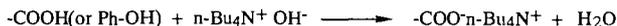


Figure 3 shows the dependence of a potential difference on the titrant volume observed in the determination of individual model compounds, benzoic acid and 2-naphthol, and that of these mixture is shown in Figure 4. Obviously, there are two inflection points on the titration curves of mixture, and it was confirmed that they were appearing at exactly right volume of the titrant corresponding to the concentration of carboxylic acid (the first inflection point) and the sum of both compounds (the second inflection point), respectively.

### 2. Non-aqueous titration of pyridine extract of coal

Based on the results obtained from the model compound experiment described above, the determination of carboxylic acid and phenolic hydroxyl functionality in the pyridine extract of Pittsburgh No.8 coal has been performed by using the same procedure. The results demonstrated in Figure 5 and 6

Comparing with model compounds experiments mentioned above, a characteristic feature seems to be the difficulty to judge one of the two inflection points, which is thought to be due to the carboxylic acid functionality in coal extract. Although the reason of this phenomenon is not clear at this moment, the indistinct pK<sub>a</sub> distribution due to heterogeneous carboxylic acid functionality in coal may be responsible for that.

Anyway, the concentration of carboxylic acid and phenolic hydroxyl functionality in the pyridine extract of Illinois No.6 coal was determined by the same manor as shown in Figure 6, and they are compared in Table 1 with those obtained from our chemical method (Aida's method) previously reported[2].

It is quite interesting that the values calculated from the two inflection points seems to be reasonably matched with those of the chemical determination. Particularly, we have convinced the matching between the sum of carboxylic acid and phenolic hydroxyl functionality determined by the chemical method (LiBH<sub>4</sub>) and the value obtained from the second inflection point, which used to be clear and have no difficulty to find out.

### 3. Non-aqueous titration of pyridine extract of coal with internal standard

In order to verify the data obtained by the non-aqueous titration, we may be able to use an internal standard compound. Namely, the addition of a standard compound, such as phthalic acid into the coal extract solution will force to shift the two inflection points with the titrant volume corresponding to the amount of the standard compound, if the identification of two inflection points was correct.

In Figure 7, the experimental results obtained were shown. Expectedly, the inflection points were shifted with exact amount of the titrant volume corresponded to phthalic acid.

### CONCLUSION

A chemical determination method (Aida's method) for the oxygen containing functionality in coal and coal product has been verified by using an alternative analytical technique, "non-aqueous titration".

It seems to be a very serious mischief concerning the content of the carboxylic acid functionality in higher rank coals than sub-bituminous coal in previous literatures, which used to be reported as a almost negligible amount. In according with our chemical determinations the content of carboxylic acid functionality in Illinois No.6 coal reach up to 5times more than previous data.

### ACKNOWLEDGEMENTS

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- (7) After irradiation with ultrasonic wave for 3hours at room temperature, the suspension of powdered coal and excess amount of piridine was filtrated by using the Memblem Filter (5 $\mu$ m) under pressure.

Table 1. Functionality analyses of pyridine extract of Illinois No.6 coal

Functionality	Aida's method		Non-aqueous titration	
	(mmol / g)			
-COOH	0.83	(n-Bu <sub>4</sub> NBH <sub>4</sub> )	0.88	(1st inflection point)
Ph-OH + -COOH	2.90	(LiBH <sub>4</sub> )	2.76	(2nd inflection point)

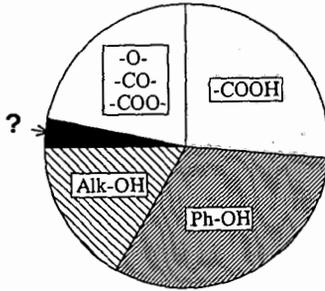


Figure 1. Distribution of oxygen functionality in pyridine extract of Illinois No.6 based on total oxygen

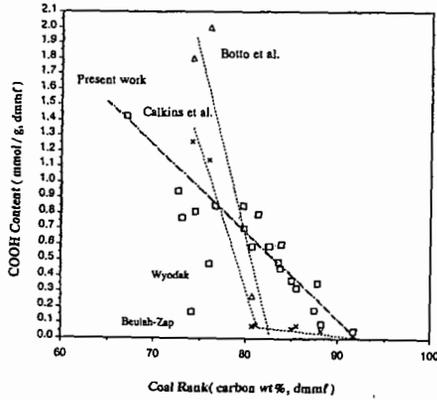


Figure 2. Correlation between content of carboxylic acid functionality and coal rank

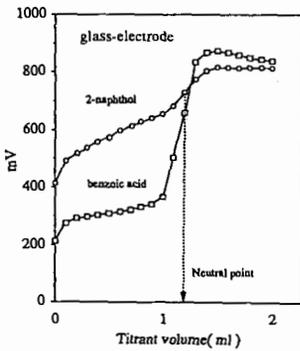


Figure 3. Non-aqueous titration of model compound

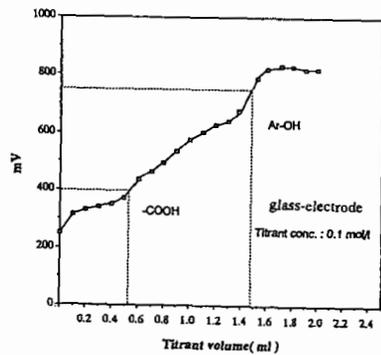


Figure 4. Non-aqueous titration of model compound mixture

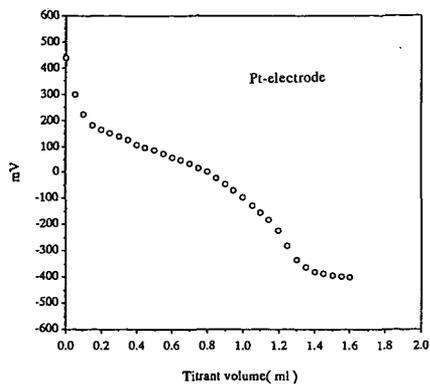


Figure 5. Non-aqueous titration of pyridine extract of Pittsburgh No.8

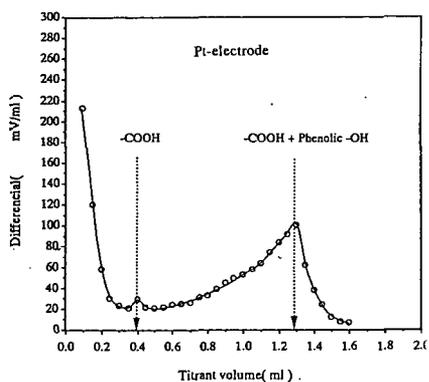


Figure 6. Non-aqueous titration of pyridine extract of Pittsburgh No.8

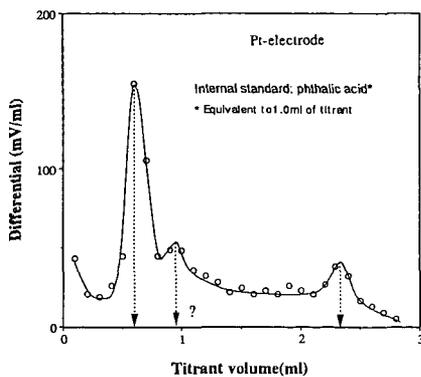


Figure 7. Non-aqueous titration of pyridine extract of Pittsburgh No.8 with internal standard