

RING ANALYSIS OF HIGH OXYGEN CONTENT SAMPLES;  
A MODIFICATION OF THE *n*-*d*-*M* METHOD

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Ring analysis of hydrocarbon samples is a technique of longstanding use. The *n*-*d*-*M* method of VanNes and VanWesten is one of the time-tested procedures (6). Hazelwood has presented a modification of this method for use with highly aromatic samples (3).

However, no ring analysis method has ever been reported for high oxygen content samples. Such materials are not infrequently encountered in various fields of research. In work on low-temperature coal tars, various oxygen containing fractions are obtained, such as tar acids containing phenolic compounds, neutral oils containing aromatic ethers, and pitch resins, containing both phenolic hydroxyl and aromatic ether groups.

This paper describes a modification of the *n*-*d*-*M* method that makes it possible to obtain acceptable ring analyses of high oxygen content samples in which the oxygen is present in aromatic ether groups and/or phenolic hydroxyl groups. This modification is based on the comparison of the refractive indices and densities of a very large number of oxygen compounds with the values for the structurally analogous hydrocarbons. The physical properties of over 1200 oxygen compounds have been gathered. Those for low-boiling phenols have been published (4); a similar list for aromatic ethers will appear shortly as a Bureau of Mines publication. The values for the analogous hydrocarbons are available from current American Petroleum Institute data sheets (1) and Egloff (2).

The applicability of this modification is demonstrated with a variety of samples of known ring contents. These samples consist of synthetic blends of pure aromatic oxygen compounds, the refractive indices and densities being determined experimentally on the mixtures.

DERIVATION OF EQUATIONS

With an increasing proportion of alkyl groups the refractive index and density of aromatic hydrocarbons and their oxygen analogs gradually change toward the values for the limiting paraffin or paraffin of infinite molecular weight, namely,  $n_D^{20}$  1.475 and  $d_4^{20}$  0.851. (Both normal and branched alkyl groups through butyl were included in the present study, that is, all isomers for which data were available.) The rate of this change is approximately linear with respect to the reciprocal of the molecular weight, and may be expressed as follows:

$$\frac{dn}{dM} = \frac{n_D^{20} - 1.475}{1000/M} \quad (1)$$

$$\frac{dd}{dM} = \frac{d_4^{20} - 0.851}{1000/M} \quad (2)$$

The average refractive index or density for the isomers of a given molecular weight, if inserted in the appropriate equation along with the molecular weight, will give the rate of change. With the refractive index and density at several molecular weights the degree of linearity may be observed and the average rates for a class of oxygen compound (O), and its analogous hydrocarbon (H), may be obtained. The notations for these are as follows:

$$\left(\frac{dn}{dM}\right)^O ; \left(\frac{dd}{dM}\right)^O \tag{3}$$

$$\left(\frac{dn}{dM}\right)^H ; \left(\frac{dd}{dM}\right)^H \tag{4}$$

The difference between the refractive index or density of an oxygen compound mixture and its analogous hydrocarbon mixture at a given average molecular weight may be obtained from the following equations:

$$\Delta n_D^{20} = \frac{1000}{M} \left[ \left(\frac{dn}{dM}\right)^O - \left(\frac{dn}{dM}\right)^H \right] \tag{5}$$

$$\Delta d_4^{20} = \frac{1000}{M} \left[ \left(\frac{dd}{dM}\right)^O - \left(\frac{dd}{dM}\right)^H \right] \tag{6}$$

These may be expressed with the simpler notation of proportionality constants, in the following manner:

$$\left[ \left(\frac{dn}{dM}\right)^O - \left(\frac{dn}{dM}\right)^H \right] = k_n \tag{7}$$

$$\left[ \left(\frac{dd}{dM}\right)^O - \left(\frac{dd}{dM}\right)^H \right] = k_d \tag{8}$$

The differences shown in Equations 5 and 6 would be less when considering mixtures consisting only in part of oxygen compounds. In this instance the difference is decreased by the factor OM/1600, where O is the weight percent of oxygen. The final equations for determining the change in refractive index or density in going from an oxygen compound mixture to the structurally analogous hydrocarbons are as follows:

$$\Delta n_D^{20} = k_n \frac{O}{1.6} = k_n^* O \tag{9}$$

$$\Delta d_4^{20} = k_d \frac{O}{1.6} = k_d^* O \tag{10}$$

#### DETERMINATION OF PROPORTIONALITY CONSTANTS

The rates of change of refractive index and density with molecular weight for 11 different classes of oxygen compounds and the structurally analogous hydrocarbons are presented in Table I. The average physical properties of the isomers at various molecular weights, from which the rates were determined, are also given.



(Table I - Continued)

Chromans		Analogous Tetralins	
134	7.46	132	7.58
	1.544		1.541
148	6.75	146	6.85
	1.538		1.537
162	6.17	160	6.25
	1.535		1.530
176	5.68		0.948
	1.529		0.0088
190	5.26		0.016
	1.527		
	0.986		
	0.0099		
	0.0095	avg.	0.0088
	0.027		0.016
Benzofurans		Analogous Indenes	
146	6.85	144	6.94
	1.548		1.544
174	5.75	172	5.82
	1.535		0.958
	1.009		0.0099
	0.0104		0.018
	0.027	avg.	0.0099
	0.027		0.017
Benzopyrans		Analogous Dihydronaphthalenes	
132	7.58	130	7.69
	1.566		1.559
146	6.85	144	6.94
	1.557		0.990
160	6.25	158	6.33
	1.552		0.977
	1.036		0.0111
	0.0123		0.020
	0.030	avg.	0.0110
	0.030		0.020
Phenols		Analogous Alkylbenzenes	
122	8.20	120	8.34
	1.538		1.504
136	7.35	134	7.46
	1.531		1.503
150	6.67	148	6.76
	1.521		0.876
164	6.10	162	6.17
	1.521		1.499
	0.978		0.874
	0.021		0.0039
	0.021	avg.	0.0038
	0.021		0.0036
Dialkylbenzenes		Analogous Alkylbenzenes	
152	6.58	148	6.76
	1.524		1.500
166	6.02	162	6.17
	1.515		1.496
180	5.56	190	5.26
	1.515		1.494
194	5.16		0.870
	1.509		0.0036
	0.991		0.0036
	0.066	avg.	0.0036
	0.027		0.0034
	0.029		0.0037
	0.029		0.0034
Catechols		Analogous Alkylbenzenes	
124	8.06	120	8.34
	1.570		1.509
138	7.25	134	7.46
	1.561		1.508
152	6.58	148	6.76
	1.098		1.506
	0.038		0.882
	0.040	avg.	0.0044
	0.040		0.0044
	0.040		0.0044

The proportionality constants  $k_n$  and  $k_d$  were determined from the differences in the rates, as indicated in Equations 7 and 8, and these are presented in Table II. The values of  $k_n^*$  and  $k_d^*$  indicate the increase in refractive index and density for each 1 percent increase in oxygen content of the sample as compared to the structurally analogous hydrocarbons.

#### EXPERIMENTAL

A variety of samples of known ring contents were examined. These consisted of pure oxygen compounds and their synthetic blends. All of the blends were liquids, although in some instances individual components, like dibenzofuran, were solids.

The physical properties were determined on these samples by semimicro methods essentially the same as those described by Sullivan, Fries, McClenahan, and Willingham (5). The resulting values of  $n_D^{20}$  and  $d_4^{20}$  are given in Table III.

The values of  $\Delta n_D^{20}$  and  $\Delta d_4^{20}$  were determined from Equations 9 and 10, using the known oxygen contents and the average  $k_n^*$  and  $k_d^*$  for either aromatic ethers or phenolic compounds. These values were subtracted from the experimental values of refractive index and density, respectively, in order to obtain the approximate physical properties of the structurally analogous aromatic hydrocarbons. The ring analysis method of Hazelwood (3) for highly aromatic hydrocarbon samples was then applied. The resulting values for total rings,  $R_T$ , and aromatic rings,  $R_A$ , are presented in Table III. The ring analysis values found without taking the oxygen content into consideration are given in parentheses. The known ring contents are given for comparison.

#### DISCUSSION

The ring contents found by the modified method agree well with the known values for both synthetic blends of oxygen compounds and individual constituents. On the other hand, if it is assumed that there is no oxygen present, ring contents are found which are very much different from the known values.

The small discrepancies observed with the modified method are probably as much owing to the inherent limitations of the Hazelwood method (at least for pure compounds and their simple mixtures) as to the small errors inherent in the modification. In all instances in which it is assumed that there is no oxygen present the values of  $R_T$  are much too large while the values of  $R_A$  are much too small. With the modified method the values of  $R_T$  are just slightly too large while the values of  $R_A$  are slightly too small.

In some instances it may be desired to obtain ring analyses on samples which contain both aromatic ethers and phenolic compounds in an undetermined ratio. Since the effect of oxygen in either form is up to ten times greater for density than for refractive index the values of  $k_d^*$  are of primary significance. A mixture with a small proportion of phenolic compounds would require a  $k_d^*$  of about 0.008 whereas a mixture with a large proportion of phenolic compounds would require a  $k_d^*$  of about 0.010. The aromatic ether  $k_d^*$ , 0.007, and the phenolic compound  $k_d^*$ , 0.011, give an average value of 0.009. This differs by only 0.001 from the values of 0.008 and 0.010 mentioned previously. Therefore, the average  $k_d^*$ , 0.009, could be used for an unknown mixture of aromatic ethers and phenolic compounds.

Table II. Proportionality Constants for Use  
in Equations 9 and 10

<u>Oxygen Compound Class</u>	<u><math>k_n</math></u>	<u><math>k_n^*</math></u>	<u><math>k_d</math></u>	<u><math>k_d^*</math></u>
Aromatic Ethers:				
Monoalkoxybenzenes	0.0013	0.0008	0.011	0.007
Dialkoxybenzenes	$0.0034/2^a$	0.0011	$0.026/2^a$	0.008
Alkenoxybenzenes	0.0013	0.0008	0.010	0.006
Phenoxybenzenes	0.0007	0.0004	0.009	0.006
Alkoxynaphthalenes	0.0011	0.0007	0.011	0.007
Dihydrobenzofurans	0.0011	0.0007	0.012	0.008
Chromans	0.0007	0.0004	0.011	0.007
Benzofurans	0.0007	0.0004	0.010	0.006
Benzopyrans	0.0011	<u>0.0007</u>	0.010	<u>0.006</u>
	avg.	0.0007	avg.	0.007
Phenolic Compounds:				
Phenols	0.0037	0.0023	0.017	0.011
Catechols	$0.0075/2^a$	<u>0.0023</u>	$0.036/2^a$	<u>0.011</u>
	avg.	0.0023	avg.	0.011

a. Divided by 2 since there are two oxygen atoms per molecule.

Table III. Experimental Results on Pure Oxygen Compounds and Their Mixtures

Sample No.	Components	Mole %	Oxygen, Wt. %	$n_D^{20}$	$d_4^{20}$	M	Found <sup>a</sup>		Known	
							RT	RA	RT	RA
1	Isochroman 2-Methyl-2,3-dihydrobenzofuran Dibenzofuran	33.3	10.99	1.5698	1.0849	145.50	2.4 (3.3)	1.1 (0.7)	2.3	1.3
		33.3								
		33.3								
2	Phenyl Ether Dibenzyl Ether Dibenzofuran	33.3	8.95	1.5887	1.0824	178.87	2.7 (3.6)	1.5 (1.1)	2.3	2.0
		33.3								
		33.3								
3	1-Methoxynaphthalene Isochroman 2-Methyl-2,3-dihydrobenzofuran	33.3	11.25	1.5682	1.0711	142.18	2.2 (3.1)	1.1 (0.8)	2.0	1.3
		33.3								
		33.3								
4	2,4-Dimethylphenol 2-Ethylphenol 3-Ethylphenol	33.3	13.10	1.5340	1.0196	122.16	1.2 (2.5)	0.9 (0.5)	1.0	1.0
		33.3								
		33.3								
5	Isochroman	100	11.93	1.5450	1.0736	134.17	2.2 (3.1)	1.3 (0.4)	2.0	1.0
6	2-Methyl-2,3-dihydrobenzofuran	100	11.93	1.5301	1.0275	134.17	1.9 (2.7)	0.8 (0.4)	2.0	1.0
7	3-Ethylphenol	100	13.10	1.5297	1.0095	122.16	1.1 (2.4)	0.9 (0.5)	1.0	1.0
8	2,4-Dimethylphenol	100	13.10	1.5320	1.0249	122.16	1.2 (2.5)	0.8 (0.5)	1.0	1.0

a Values in parentheses were obtained assuming no oxygen present.

## LITERATURE CITED

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