MINIMUM FORMULA WEIGHT OF HUMIC SUBSTANCES

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INTRODUCTION

Formula weights are formulated from known elemental compositions and in chemistry often used to express molecular weights. Since the advent of humic acid science, formula weights have attracted considerable attention in this branch of science, acquiring during the years the notoriety of molecular weights in defining humic acids. In previous publications Piccolo (2002) and Tan (2003; 2011a and b) have addressed in some detail the alleged failure in finding a magical number for molecular weight as one major reason to question the nature of humic substances. At one time a great number of scientists even doubt their existence in nature by calling them operational or fake compounds, and were it not for their ubiquitous presence in the earth ecosystems, humic acid science may perhaps have taken a wrong turn. It was perhaps Berzelius in 1839, followed by Mulder in 1840, who presented the first formulas for their ulmic, crenic and apocrenic acids. Using today's chemical notations, the compounds above are assigned the formula weights of $C_{20}H_{14}O_6$, $C_{12}H_{12}O_8$ and $C_{24}H_{12}O_{12}$, respectively. This is then the start for arguments, turning into a full-blown controversy, when more formulas are proposed during the development of humic acid chemistry over the years into a modern science. Unfortunately, the differences in opinions have polarized the scientific community, causing a division into two groups, with one group firmly believing in and the other group highly skeptical about the existence of formula weights for humic substances. Regardless of the convictions from the nonbelievers, several methods have been proposed by the group of believers for the construction of molecular weight formulas of humic substances. For example, Steelink (1985) has published his idea for the construction of such a structural formula. However, more modern methods are reported by Schnitzer (1994) and Schulten (1995; 1996), who apply sophisticated procedures, e.g., pyrolysis-field mass spectrometry and Curie-point pyrolysis-gas chromatography, in their quest for molecular weight formulas. Unfortunately, not only are these methods mind boggling, but the analytical instruments are also extremely expensive. Less complex, but similarly controversial, are those proposed by Steelink (1985) and Orlov (1985), presented below more coherently from the bits and pieces gathered from the articles.

THE THEORY OF MINIMUM MOLECULAR WEIGHT

.Both Steelink (1985) and Orlov (1985) have used elemental composition expressed in atomic percentages and atomic ratios for the calculation of formula weights of humic substances. In contrast to Steelink (1985), who considers only C, H, and O, Orlov (1985) also includes N in the formulations. Orlov also assumes the humic substances to be characterized by a *minimum molecular weight*, defined as the smallest possible formulation of molecular weights. The method — presented below as an illustration for calculations of an empirical formula of humic acids — is a hybrid procedure adapted from both Steelink's and Orlov's proposals. The elemental atomic percentages and atomic ratios are *not fictional* but data obtained from actual analyses of natural humic substances as reported by Tan (2003, Tables 5.2 and 5.3), extracted from 23 soil samples collected from over the world. In addition similar data of humic acids from 17 soil samples collected in Russia by Orlov (1985, Table 9) are used for comparisons and/or supporting data. The range and average atomic ratio values from Tan's data listed below are used for calculations:

Atomic Ratio	Range (*Tan*)	Average	Range (*Orlov*)	Average
H/C	0.8 – 1.2	1.0	0.8 – 1.2	1.0
O/C	0.4 – 0.6	0.5	0.4 – 0.5	0.5
N/C	0.05 – 0.07	0.06	0.04 – 0.08	0.06

As can be noticed, the average values of Orlov and Tan for H/C and O/C are very similar. They are also not different from those reported by Steelink (1985). It could be coincidental, but the stunning similarities from three independent analyses by scientists with no contact with each other tend to enforce the idea on the existence of a definite elemental composition characteristic for humic substances.

The above atomic ratio averages mean that for every carbon, there are one hydrogen, 0.5 oxygen and 0.06 atoms of N, resulting into a *working formula* of $\mathbf{C_1H_1O_{0.5}N_{0.06}}$. By rules in chemistry, formula notations should carry whole numbers instead of broken numbers, by either adjusting with a factor or rounding up to the next higher whole number. Hence, conforming to Orlov's (1985) suggestion the smallest number appearing in the working formula as 0.06, the subscript of N, has to be adjusted by a factor of 1/0.06 = 16.7 to equal 1 as shown below:

0.06 N	→ $C_1H_1O_{0.5}N_{0.06}$	
One N	$C_{16.7}H_{16.7}O_{(0.5x16.7)}N$ or rounded up: $\mathbf{C_{17}H_{17}O_8N}$	→ mol.wt = 363
Two N	$C_{34}H_{34}O_{16}N_2$	mol.wt = 726
Three N	$C_{51}H_{51}O_{24}N_3$	mol.wt = 1089
30 N	$C_{510}H_{510}O_{240}N_{30}$	mol.wt = 10690

The subscripts of C, H, and O have then to be adjusted accordingly and the broken subscript numbers rounded-up, giving a formula weight of $\mathbf{C_{17}H_{17}O_8N}$, as shown above. This is called the *minimum molecular weight* of the humic substance.

MINIMUM WEIGHT AS A HUMIC MATTER PROPERTY

As can be noticed above, the minimum molecular weight corresponds to the simplest formula and the real (total) values are then multiples of this minimum formula weight value. The usefulness to represent molecular weights depends highly on the reliability, accuracy and precision of elemental analysis. Minimum molecular formulas are in fact very common issues in the chemistry of natural biopolymers, such as with carbohydrates which exhibit a minimum molecular weight expressed by the formula $C_6H_{12}O_6$ or with protein by a minimum weight formula of $C_2H_5O_2N$ (glycine). The total carbohydrate or protein molecule is then the multiples of either $C_6H_{12}O_6$ or $C_2H_5O_2N$. The method above is much simpler than that of Schnitzer (1994) and Schulten (1996), who presented with high-tech procedures a formula of $C_{308}H_{328}O_{90}N_5$ for humic acids. It has to be admitted, though, that their goal was to discover the "true" formula. The authors also claim their formula above to correspond with an elemental composition (by wt) of 66.8%C, 6.0%H, 26.0%O and 1.30%N. Unfortunately the extremely high %C and very low %O are out of range for values reported for humic substances (Stevenson, 1998: Schnitzer and Khan, 1972). The low value for N gives also a C/N ratio = 66.8/1.3 = 51.4, which is far too high for humic acids.

The theory of minimum formula weight will perhaps increase in scientific value when its procedural concept is extended to also include the functional group —phenolic-OH and COOH groups — contents, but this is another intriguing story the author reserved for another time. To avoid the current article to become cumbersome, heavy to read and very complex, readers are invited kindly to read the author's 2003 book *Humic Matter in Soil and the Environment, Principles and Controversies*, Marcel Dekker, Inc., where some is covered in Chapter 5.

CONCLUSION

A method on minimum formula weight formulation is presented in a coherent way. It is simply written by the author from bits and pieces collected from published books and articles. It is proposed for people to contemplate or build on it better concepts that can propel humic acid chemistry into new dimensions. The idea above is indeed controversial for some in the western hemisphere, but may fill the void for the lack of a general molecular weight characterizing humic substances. As discussed above, the empirically determined minimum molecular weight formula of $C_{17}H_{17}O_8N$ corresponds to the simplest formula. The real (total) formula weights are then the multiples of this minimum formula weight value, such as exemplified by $C_{510}H_{510}O_{240}N_{30}$, which corresponds to a molecular weight = 10,690, approaching the lower limits often reported for molecular weights of humic acids. They are based on a more solid scientific foundation than $C_{308}H_{328}O_{90}N_5$ suggested by Schnitzer and Schulten. Since, the data used are not fictional, but are real data obtained from research analyses of humic substances extracted from soil samples collected world-wide, it is hoped that the concept may be viewed from a brighter perspective. The stunningly similarities of the humic acids elemental data published in Russia and the United States may testify of the presence for an elemental composition characterizing humic substances. The inclusion of functional groups — carboxyl, COOH, and phenolic-OH groups — into the formulation may perhaps also help elevating the significance level of minimum formula weights another notch.

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