TWO- AND THREE-DIMENSIONAL VAN KREVELEN DIAGRAMS: A GRAPHICAL ANALYSIS COMPLEMENTARY TO THE KENDRICK MASS PLOT FOR SORTING ELEMENTAL COMPOSITIONS OF COMPLEX ORGANIC MIXTURES BASED ON ULTRAHIGH-RESOLUTION BROADBAND FOURIER TRANSFORM ION CYCLOTRON RESONANCE MASS MEASUREMENTS

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Introduction

Ultrahigh-resolution electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry has resolved and identified the elemental compositions of over 10 000 organic constituents of coal and petroleum crude oil. A plot of Kendrick mass defect versus Kendrick nominal mass sorts compounds into homologous series according to compound class (i.e., numbers of N, O, and S heteroatoms), type (number of rings plus double bonds), and degree of alkylation (number of CH2 groups), to yield unique elemental assignments from ultrahigh-resolution mass measurements in the 200-900 Da range. Interpretation of such a vast compilation requires a simple (preferably graphical) means to differentiate between complex organic mixtures of different origin or processing. In an extension of the recently revived van Krevelen plot, each elemental composition is projected onto two or three axes according to its H/C, O/C, and/or N/C atomic ratios. The H/C ratio separates compounds according to degree of saturation, whereas O/C or N/C ratios separate according to O and N classes. We show that the three dimensional van Krevelen diagram can completely separate different classes in pyridine-extracted coal or petroleum samples and can also graphically distinguish fossil fuels according to their nature (coal vs petroleum), maturation (coals of different rank), and processing (the same coal at two stages of liquefaction). The van Krevelen diagram thus appears well suited to amplifying and exposing compositional differences within and between complex organic mixtures.1

Results and Discussion

The Figure is a three-dimensional van Krevelen diagram for the same classes (N, NO, and NO2) for two different fossil fuels: coal (blue) and crude oil (red). Because the coal components are more aromatic than are the constituents of crude oil, the two fuels are readily distinguished graphically in the diagram, even though both coal and crude oil contain molecules of the same classes and types.

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References