Analysis of long-chain alkenones by GC-MIP-AED and problems arising from different extraction techniques

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Analysis of long-chain alkenones (abbreviations as in Fig. 1) have been performed using GC-FID, GC-MS and GC-irmMS systems. Here the application of a gas chromatograph - microwave induced plasma - atomic emission detector coupling (Quimby and Sullivan, 1990) is described. Special feature of this detector is the ability to record chromatograms at different wavelengths specific for each element at the same time (e.g. C, H, O, N, S). Depending on the intensity of the chosen emission lines, sensitivity is enhanced in comparison to FID for carbon and surpasses the MS for some elements. Routine use of the GC-MIP-AED is made in environmental geochemistry in analysing organo-metallic compounds, PCBs and pesticides. Because of its capability to determine elements occurring in eluting compounds and therefore offering empirical formulas it is used as a complementary system to GC-MS in samples with complex matrices.

Results

Optimization of AED-parameters for the detection of carbon (C 496 nm), hydrogen (H 486 nm) and oxygen (O 777 nm) yielded values for gas flow rates, transfer and cavity temperatures as summarized in Table 1.

TABLE 1. Optimized AED-parameters used

	C + H	O 777
He Makeup flow [ml/min]	50	100
O_2-reagent gas [bar]	1.4	OFF
H_2-reagent gas [bar]	4.0	2.1
N_2+CH_4-auxilliary [bar]	OFF	2.0
Transfer line temp [°C]	335	335
Cavity temp [°C]	350	350

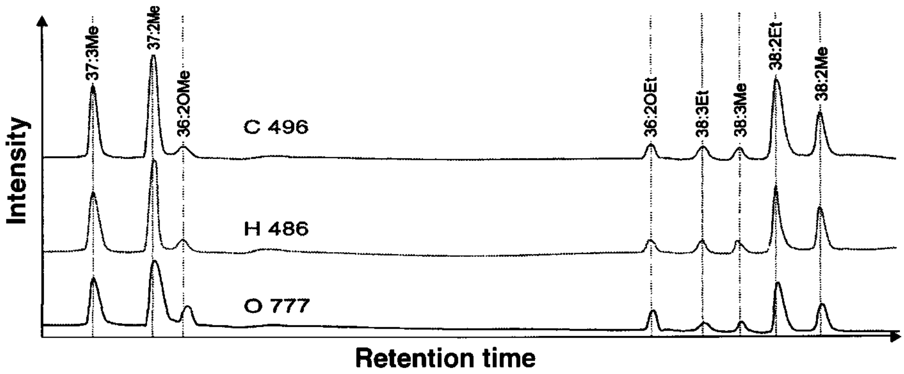

FIG. 1. Example of a composite C, H, O chromatogram of the alkenone and alkenoate fraction. Note the relative raise of peak areas of 36:2OMe and 36:2OEt in the O 777 trace. Abbreviations: 37:3Me = heptatriaconta-8E,15E,22E-trien-2-one; 37:2Me = heptatriaconta-15E,22E-dien-2-one; 36:2OMe = methyl hexatriaconta-14E,21E-dienoate; 36:2OEt = ethyl hexatriaconta-14E,21E-dienoate; 38:3Et = octatriaconta-9E,16E,23E-trien-3-one; 38:3Me = octatriaconta-9E,16E,23E-trien-2-one; 38:2Et = octatriaconta-16E,23E-dien-3-one; 38:2Me = octatriaconta-16E,23E-dien-2-one.

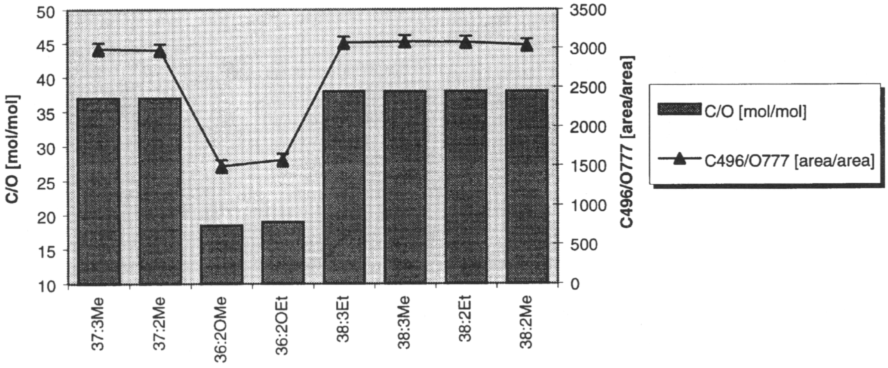

FIG. 2. Comparison of theoretical atomic C/O ratios with quotients of measured C 496 and O 777 areas of alkenones and alkyl alkenoates.

As an example a composite chromatogram for C, H and O of the alkenone and alkenoate fraction is shown in Fig. 1. In addition to the enhanced sensitivity, the GC-AED offers the possibility of testing for coeluting compounds, in the case of alkenones for instance by wax esters or partly by insufficient peak separation of alkenones and alkyl alkenoates.

In Fig. 2 the calculated atomic C/O ratios of alkenones and alkyl alkenoates in elution order are plotted along with the measured area/area quotients. Evident are the large variations in C/O ratios, e.g. comparing 37:2Me and 36:2OMe, which enables detection of possible contributions of 37:2Me to the 36:2OMe peak area and vice versa. Calculation of the C 496/O 777 [area/area] quotients allows even the determination of the percentages of both compounds in poorly resolved peaks with a standard derivation of 2%. For example a measured C 496/O 777 value converted in a C/O ratio of 20 means a 7.5% contribution of 37:2Me to the 36:2OMe C 496 peak area. Thus, corrected peak areas can be calculated.

Further applications of the GC-AED for analysis of extractable organic matter from sediments, especially compounds containing heteroatoms, are currently developed. A recently published example (Rolfes and Andersson, 1997) is the quantification of trace amounts of alcohols and phenols by complexation of the hydroxygroup with a ferrocenecarboxylic acid containing the strongly emitting iron. This greatly enhances sensitivity down to 0.2 pg/s and offers excellent selectivity.

Effects of extraction method, of fractionation by silica-gel chromatography, of derivatization and of discrimination during the GC run on alkenone concentrations and the resulting Uk37′ values have been investigated in an intralaboratory comparison. More susceptible to changes in methodology than the Uk37′ proved the absolute concentration of alkenones. Detailed information will be available in the Internet at http://www.geol.uni-erlangen.de/coh/alkenon/ from the 30th of August 1998 on. For the use of alkenone accumulation rates as possible palaeoproductivity proxy of a single producer group (Prahl *et al.*, 1993) for the most part standardized protocols of extraction should be envisaged in order to minimize erroneous interlaboratory variations.

References

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