



The chemothermal oxidation BC method: evaluation of ex situ pretreatments, matrix-catalyzed effects, standard addition approaches, and thermal stability of various black carbons

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The highly condensed products and residues of incomplete combustion of biomass and fossil fuel termed black carbon (BC) partake in a multitude of important geochemical processes. However, ambiguity persists since different quantification methods give highly variable results, leaving it unclear whether this reflects method difficulties or that different methods simply mirror different parts of the BC spectrum. The wet chemical pre-treatment – wet chemical oxidation (wet-wet) methods (e.g., Wolbach and Anders, 1989; Verardo, 1997; Masiello et al., 2002; Song et al., 2002) have the advantage over thermal oxidation methods that there is a lower risk of charring. However, the extensive handling of samples in liquid solutions may lead to losses of BC particles, which, due to their hydrophobic character, tend to adsorb to inner surfaces of test tubes and to the water-air interface (e.g. Gélinas et al., 2001; Elmquist et al., 2004). Underestimation of total BC can also occur when the thermal energy applied during the combustion step is higher than the stability of some BC constituents.

Here we further evaluate and develop the chemothermal oxidation (CTO) approach (Gustafsson et al., 1997; 2001; Elmquist et al., 2004), which is perhaps the most commonly applied method for quantification of BC in sediments. The CTO-375 method involves 18 h thermal oxidation at 375°C of small and well-ground samples in active airflow to oxidize organic matter, and micro-acidification *in situ* in Ag capsules to remove carbonates followed by quantification of the residual carbon as BC using elemental analysis. Standard additions of incremental amounts of pure diesel soot (NIST standard reference material 2975) to four different sediments resulted in 14% to 52% lower estimates of sedimentary BC concentrations compared with the ordinary CTO-375 method (Elmquist et al., 2004). The linear standard addition slopes suggested that 38%, 51%, 78% and 101% of added SRM-2975 BC was accounted for. Separate experiments supported the notion that the somewhat lower recovery of the BC in the matrix-associated additions, compared to when run as pure standards, could be caused by either a smearing effect or a mineral-oxide catalyzed oxidation of the BC (Elmquist et al., 2004). Lowering of the combustion temperature may prove useful to compensate for these effects.

The stability of different BC types (diesel soot SRM-2975, n-Hexane soot, Wood char and Grass char) was tested in a thermogram study where laboratory produced BC materials (from BC ring trial) were combusted at various temperatures. A model-deduced estimation of the temperature when 50% carbon remained in the residue ($T_{50\%}$) reflects the thermal stability of the material. $T_{50\%}$ of the tested BC materials was as follows: 392° (SRM-2975), 369° (n-Hexane), 314° (Wood char) and 241° (Grass char). These further laboratory-based testing of the CTO-375 method combines with field-based evaluations (Gustafsson et al., this symposium) to suggest that the CTO-375 method appears generally applicable to the quantification of soot-BC in sediments. For quantitative estimates of also the more labile char-BC components, complementary approaches are required (e.g., Cornelissen et al., 2004; Quénea et al., this symposium).

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