A dedicated sampling and measurement method was developed for long-term measurements of biogenic and fossil-derived CO₂ from thermal waste-to-energy processes. Based on long-term sampling of CO₂ and ¹⁴C determination, plant-specific emission factors can be determined more accurately, and the annual emission of fossil CO₂ from waste-to-energy plants can be monitored according to carbon trading schemes and renewable energy certificates. Weekly and monthly measurements were performed at five Danish waste incinerators. Significant variations between fractions of biogenic CO₂ emitted were observed, not only over time, but also between plants. From the results of monthly samples at one plant, the annual mean fraction of biogenic CO₂ was found to be 69% of the total annual CO₂ emissions. From weekly samples, taken every 3 months at the five plants, significant seasonal variations in biogenic CO₂ emissions were observed (between 56% and 71% biogenic CO₂). These variations confirmed that biomass fractions in the waste can vary considerably, not only from day to day but also from month to month. An uncertainty budget for the measurement method itself showed that the expanded uncertainty of the method was ± 4.0 pmC (95% confidence interval) at 62 pmC. The long-term sampling method was found to be useful for waste incinerators for determination of annual fossil and biogenic CO₂ emissions with relatively low uncertainty.