

AN OVERVIEW OF A RELATIVELY SIMPLE METHOD TO DETERMINE THE BIOGENIC VERSUS FOSSIL FUEL COMPONENT OF A SOURCE EMISSION: BS ISO 13833: 2013

In this world, the origin of waste is becoming increasingly important to operators who dispose of waste. Often, taxation on the disposal of waste is based on its biogenic credentials. Rebates are sometimes given where energy is produced from sustainable renewable biomass or biogenic material. For waste sites, biogenic materials may be taxed very differently from non-biogenic materials.

As producers of goods get more adept at producing products either wholly from biogenic sources or from a mixture of biogenic and renewable sources, the difficulty in distinguishing between material that is fossil fuel based or biogenic based is becoming increasingly difficult; and yet there are fiscal reasons to distinguish the biogenic make up of waste materials.

The standard methods are:

1. All the material is CO₂ Neutral; this is ideal where the waste stream all arises from a single known sources such as biomass e.g. straw, willow etc.

2. Selective Dissolution Method (SDM); a small fraction of the waste is treated with an oxidising agent, typically a mixture of hydrogen peroxide and sulphuric acid. The biomass fraction is oxidised faster than non-biomass fractions and hence the amount of biomass can be calculated after correcting for moisture, inert materials (such as ash) and the amount of carbonates present.

3. The Reductionist Method; this can be applied where the biomass content is in the range 20-80%. It doesn't work well where there are high calorific contents in the waste (such as fats). The calorific value (CV) of the fuel is determined along with the ash content, and moisture content. Then, knowing the CV of individual constituents of the waste, the percentage biomass can be calculated. Unsurprisingly this works well where the contents of the waste stream are well defined/characterised.

Based on the ¹⁴C values measured in the summer of 2011 at measurement site Lutjewad (NL), a pmC value of 104 % for biomass grown and harvested in the period of 2010-2012 is obtained (oral communication with S. Palstra dated 2011-11-07).

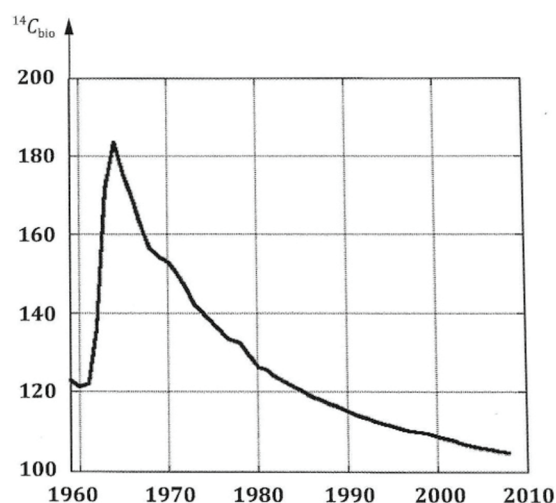


Figure 1 - Decrease in ¹⁴C_{bio} value in the atmospheric air CO₂ (in pmC), measured at high Alpine stations Vermont (Austria) and Jungfrauoch (Switzerland) (see Reference [1]); for data 2004- 2008: personal communication S.Palstra with I. Levin)

[1] Levin I. & Kromer B.: Radiocarbon 2004, 46, pp1261-1272

4. The Manual Sorting Method; the waste is sorted into sub-fractions and categorised. It is then sorted into material that is bigger than 1 cm, dried and weighed. The precision of this method can be assessed using the SDM method discussed earlier. This should be carried out in triplicate. Any significant differences in the SDM results suggest that either the sorting method is poor or that the waste is highly heterogenous.

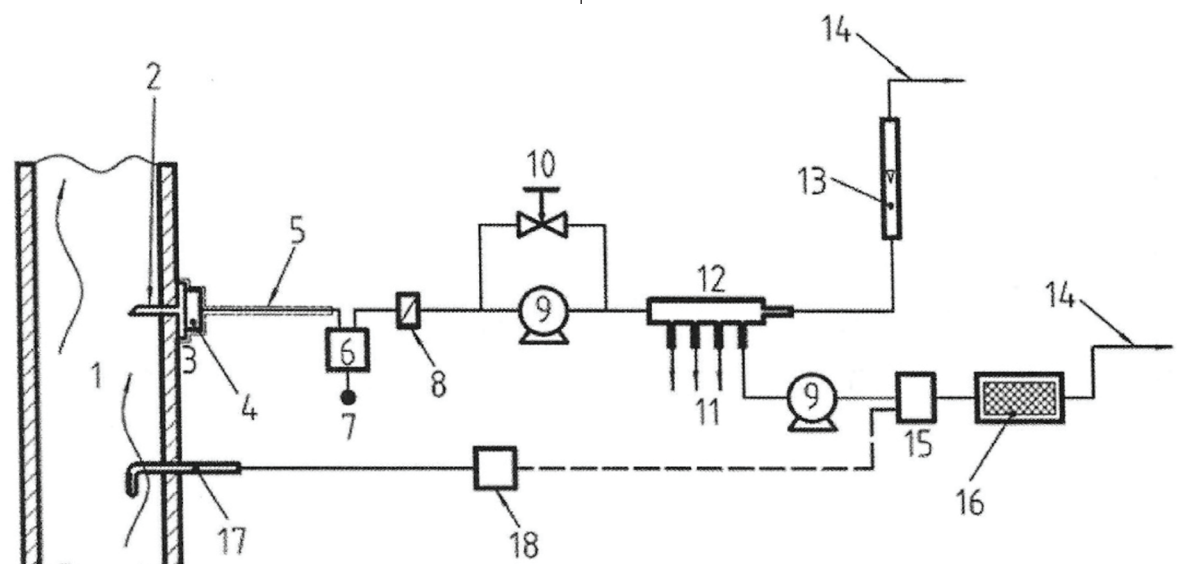
If we consider the incineration of refuse, the tax associated with the disposal of waste is becoming crucial. Furthermore, there are tax benefits from the energy regulators where it can be proven that the waste was biogenically derived. Traditionally how was this achieved?

It hasn't been a pleasant process, as anyone involved will tell you. Ideally, first take 50 tonnes of waste, then split it into a smaller amount and attempt to classify the material visually (remember this is the contents of your dustbin/wheelie bin etc.). Then aim to obtain a 10-20g sample which is representative of that waste! Once you've got the "representative sample" what next? Analyse it using the methods discussed above! Clearly, although there are Standards to help do this, the process is hugely manual and subjective. Now add to this the fact that manufacturers of plastics are aiming to make a recyclable or bioplastic which is indistinguishable from a fossil fuel-based product, and the process becomes even worse.

However, there are better ways to do this that are far more elegant. The Carbon-14 (¹⁴C) method is one such alternative. Is it difficult, dangerous, or not very good? Well, the answer to all these is no, it works really well. It relies on the fact that the naturally occurring isotope of ¹⁴C has a half-life of 5730 years. It is formed from cosmic neutrons interacting with nitrogen in the atmosphere. Plants then absorb the ¹⁴C. It is routinely used to carbon date archaeological artefacts. In addition, anything over 60,000 years old has no detectable ¹⁴C present. So, fossil fuels are devoid essentially of ¹⁴C, whilst more recent biomass has a lot of ¹⁴C relatively speaking.

Is there anything that makes the determination of ¹⁴C more difficult. Well of course there is, this is real life! In the 1950s & 1960s the nuclear weapon tests changed the natural background levels. The levels increased dramatically and have been decreasing since. The graph below shows how ¹⁴C_{bio} has changed since the 1960s. Other notable events which have affected the levels have included further nuclear weapon trials in the 1980s and the Chernobyl disaster.

It has subsequently been decided that the current level is 104-105% pmC (percentage of modern Carbon) of the ¹⁴C levels of 1950. This is accepted to be our datum.



Key

- 1 flue gas
- 2 probe
- 3 heater
- 4 primary filter
- 5 heated sample line
- 6 dehumidifier unit

7 water discharge

- 8 secondary filter
- 9 sampling pump
- 10 bypass valve
- 11 to analyser(s)
- 12 manifold
- 13 flow meter (optional)

14 exhaust

- 15 mass flow controller
- 16 CO₂ absorber (LS)
- 17 velocity measurement
- 18 flow rate meter

CO₂ Absorber can be:

- Liquid Impinger with 1mol/l NaOH or KOH
- A Caustic Solid Absorber (Ascarite II)
- Tedlar™ Gas Bag Collector

Figure 2 - Example of sampling train for proportional sampling

So how is this used to determine the biogenic fraction of waste? A simple sample of CO₂ is either collected into a large Tedlar™ bag or absorbed in an alkaline absorbent solution or solid substrate.

Figure 2 shows a typical arrangement for sampling. It is a lot simpler than might at first be thought as the sampling can be achieved using a standard AMS/CEM (automatic measuring system/continuous emission monitoring) system. The key components of the sampling system are already present where there is an extractive CEM system. It only requires a manifold and, if required, the addition of a proportional sampling pump and feedback loop to the flow measurement system. A CEMs supplier should be able to provide the necessary modifications where required. A proportional sampling system is only required if the levels of carbon dioxide (CO₂) vary dramatically (i.e., twice the coefficient of variance of the CO₂ levels is greater than 55%). A small amount of gas is obtained periodically, typically over a month and composited into the bag or absorber. The sample is recovered and sent for analysis by a specialist laboratory.

The ratio of the level of ¹⁴CO₂ to the amount of ¹²CO₂ is determined. This can then be related to the amount of biogenic waste versus that originating from fossil fuel derived plastics etc. This can be achieved by several alternative analytical methods:

Table 1: Comparison of Analytical Techniques

	Amount of CO ₂ (l)	Analysis Time	Error (StDev) pmC
AMS	0.004	Only limited by the Shipment Time	0.1-0.5
LSC (C ₆ H ₆ Synthesis)	1	Can be varied by lengthening the analysis time or conc. of solution	0.3-2
LSC by CO ₂ Absorption	Variable to meet analytical requirements	Can be varied by lengthening the analysis time or conc. of solution	2-4
β-Ionisation	2-10	2-4 days per sample	0.3-0.5

- AMS (Accelerator Mass Spectrometry) The gas bag/canister is shipped by air freight to a lab, usually in the USA. The laboratory will usually take care of all arrangements. You receive the results. They calculate ratio of ¹⁴C/¹²C or ¹⁴C/¹³C and ¹³C/¹²C. They provide the pmC. The level of 100% bio-based carbon was set at 105pmC in 2009.

- Liquid Scintillation Counting Method. LSC determines the amount of ¹⁴C indirectly through its emission of β-particles. The CO₂ is initially either converted to benzene or reacted with an amine solution to form carbamates.

- Direct β-Ionisation Detection.

The amounts of gas and the typical errors associated with the measurements by the different methods are shown in Table 1.

The ¹⁴C Method for determining the biogenic fraction of the waste has the following characteristics:

Advantages

- Simple sampling
- Provides a time averaged sample
- Can be automated so that only the absorber needs changing and shipping

Disadvantages

- The method could appear daunting initially, but actually all the hard work is done by the labs.
- Peat will be assigned as biomass erroneously.
- It is necessary to ensure that no air can get into the samples during shipping.

Given the problems associated with traditional methods, the ¹⁴C method offers some real advantages over the manual and SDM methods. It can also be used to validate computer-based balance methods such as the BIOMA software (developed by Vienna University of Technology and Ramboll) and methods based on BS ISO 18466:2016.

Dr Roger Brown FRSC is the Managing Director of Oakwood Environmental Services, an emissions and environmental consultancy. Dr Brown has been actively involved in consultancy and all aspects of source emission and ambient air testing for over 35 years. As a director of several blue-chip companies, he developed their emission test services. He currently provides consultancy to some of the world's largest companies and holds patents for the measurement of various novel species and processes. He has also designed and commissioned state-of-the-art mobile laboratories for regulatory purposes and process optimisation. He has authored numerous papers and chapters in key works on the measurement of pollutants. He graduated from Southampton University with a doctorate in chemistry and conducted postdoctoral research into mass spectrometry and dioxin analysis. He is currently a director of the Source Testing Association and was a past Chairman, having been involved in the association for 28 years.



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