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RADIOCARBON DATING

NOTES ON SERVICES PROVIDED BY

RCD - RADIOCARBON DATING

IN RESPECT OF

CARBON-14 AND TRITIUM MEASUREMENTS FOR LANDFILL GAS INVESTIGATIONS

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1.0 About the RCD-RadioCarbon Dating Laboratory

RCD (RadioCarbon Dating), was formed in 1989 by RL Otlet and AJ Walker to carry out measurements of low-level carbon-14 and tritium for environmental, industrial and archaeological applications. The laboratory routinely carries out analytical work for BNFL, Sellafield, Chapel Cross, UKAEA Harwell, UKAEA Culham (JET facilities), AWE Aldermaston and RAL. Landfill gases are also routinely measured for private companies for source identification purposes.

RCD operates from a purpose-designed laboratory, housed in premises at Lockinge, near Wantage, equipped with the necessary facilities to undertake the measurement of low activity levels of tritium using liquid scintillation counting and also low activity levels of carbon-14 measurements using the technique of benzene synthesis followed by liquid scintillation counting. RCD has also formed a link with two established accelerator mass spectrometry (AMS) laboratories abroad and sub-contracts those carbon-14 samples which, being too small for liquid scintillation counting, require this type of measurement.

Laboratory equipment at Lockinge includes four liquid scintillation counters, all Wallac Quantulus machines, for low-level tritium and carbon-14 measurements and associated apparatus for sample processing. This includes, for carbon-14, equipment for conversion of samples to benzene for counting and, for tritium, vacuum distillation equipment, freeze drier, electrolytic enrichment apparatus and a purpose built rig for combustion of samples to produce water, eg for OBT.

This document specifically concentrates on those measurements concerned with the source identification of landfill gases and leachates.

2 Carbon-14

Carbon-14 , the radioactive isotope of carbon (half-life 5570 years, max β^- energy 160 keV) is produced naturally in the upper atmosphere through the reaction of neutrons from cosmic rays with nitrogen (^{14}N n,p ^{14}C). The ^{14}C rapidly oxidises to form $^{14}CO_2$ and, as such, lies at the head of the food chain for all living organisms. While any organism is alive, the ^{14}C within it stays at a steady level but after death this begins to decay following the half-life of 5570 years giving the basis for the technique of radiocarbon dating. A significant input of ^{14}C was delivered into the atmosphere in the 1950s and 1960s during the atmospheric weapons trials, with the level of ^{14}C in the Northern hemisphere rising to nearly twice its normal level in 1963/4. Figure 1 illustrates the levels in UK organic material since 1948. Enhanced levels in atmospheric CO_2 (~10% above the pre-1950s levels) are still discernable (the 1960 levels having been largely diluted through exchange with the greater CO_2 reservoirs of the Earth's oceans).

2.1 Carbon-14 Measurement Techniques

Two methods are currently offered by RCD for carbon-14 measurement - benzene synthesis and accelerator mass spectrometry (AMS), the latter being the most suitable method if the amount of carbon in the sample is very low, ie significantly below 1g carbon. Full processing is carried out at RCD in the first of the two methods where samples pass through a procedure which produces benzene for low-level liquid scintillation counting. The smaller samples, which require the second method, are processed to CO_2 then sent to the AMS laboratory for measurement. The main features of the techniques are as follows:

1 Benzene synthesis - Combustion or acidification of the sample to CO_2 followed by conversion to benzene through the stages of lithium carbide and C_2H_2. Liquid scintillation counting of the benzene sample in an optimised low level liquid scintillation counter, eg Wallac Quantulus to achieve an overall precision of ± 1% (ie ± 2.5 Bq/kg carbon). Sample size required 1g to 4g elemental carbon.

2 Accelerator mass spectrometry - Combustion or acidification of the sample to CO_2 (at RCD) followed by conversion of the sample to graphite at an accelerator laboratory and measurement of the ^{14}C content. Measurement precision of the method is given as approximately ± 0.5% (± 1.2 Bq/kg carbon) for sample sizes greater than 1mg carbon.

3 Tritium

Tritium is the radioactive isotope of hydrogen and, as such, occurs in many forms, as part of the water molecule (HTO), in its elemental form as hydrogen gas (HT), as organically bound tritium in foodstuffs and other organic matter or in methane gas (CH_3T). The natural production of tritium is very low, in the units in which it is generally considered, probably less than 3 TU (1 TU = 0.12 Bq/*l* water). A major increase in this value occurred, however, in the 1950s and 1960s with additional input from the atmospheric nuclear tests.

Since 1964, the time of the Test Ban Treaty, the level of tritium has declined through uptake in the oceans and radioactive decay (half-life = 12.43y) and in the UK rain now is generally less than 10 TU. However, much higher levels (factor of x1000 higher) are frequently found in CH_4 from waste sites in which artificially produced ^3H has been deposited. Artificially produced ^3H was extensively used in the late 1960s to 1970s to enhance the luminosity of such items as clock and watch dials, objects which eventually turned up in landfill sites. This ^3H can then be found in landfill leachates and, by methanogenesis, into CH_4.

3.1 Tritium Measurement Techniques

Measurements of tritium can be made directly from pure water using the technique of liquid scintillation counting for levels above 25 TU. Impure (dirty or coloured) waters would, however, require a preceding distillation stage. (Below 25 TU an electrolytic enrichment procedure may be available for measurements of current natural rainwater levels or groundwater, providing enough for the process can be supplied (>175 ml)).

Measurement techniques offered by the RCD laboratory for tritium are as follows:

1 Direct counting of water sample (5 to 10 ml), with or without distillation depending upon the sample purity as supplied, in an optimised low level liquid scintillation counter (eg, Wallac Quantulus). Least detection limit 25 TU (3.0 Bq/l) with a counting time of approximately 500 min.

2 20 times enrichment of the water sample (175ml) by electrolysis, followed by liquid scintillation counting. Least detection limit 1 TU (0.1 Bq/*l*) with a counting time of approximately 500 min. (NB availability of this process is by negotiation and generally only for batches of 10 or more samples.)

4 Stable Isotope Measurements ($\delta^{13}C$)

Precise measurements of the $^{13}C/^{12}C$ ratio are made on a small aliquot of the purified CO_2 sample. For this the sample is vacuum sealed in a glass vial and sent for mass spectrometry measurement to a specialist laboratory. The results, expressed as a difference value to that of an international standard, are given as $\delta^{13}C$ in units of per mil (‰). NB 1‰ is the same as 0.1%.

5 Isotope Measurements for Landfill Applications

5.1 Carbon-14

Modern waste tips which contain organic rubbish will carry the ^{14}C levels appropriate to the time the material was living. If the composition of the rubbish is largely current organic material, eg garden waste, then these levels transmit directly to the $^{14}CH_4$ formed by their decomposition. There is, in this case, a clearly measurable difference between CH_4 originating from decomposition of matter in the waste tip and CH_4 from coal measures or oil products which do not contain ^{14}C or ^{3}H.

Values between 0% and 100% 'modern' levels are more difficult to interpret as these values may arise from mixtures of ancient and modern sources or, directly, from older peat deposits. Often this can be resolved from knowledge of the site and its environs, and, in the case of a nearby peat deposit, a specific measurement of a peat sample to establish its age may help.

5.2 Tritium

Measurement of the tritium in the water formed in the combustion of the methane is recommended in landfill gas investigations. Although, because of dilution and the shorter half life of ^{3}H (12.43y), the enhanced levels of the 1960s are no longer discernible, sources from landfill containing luminous dials of any kind activated with tritium will show a clear signal of highly enhanced tritium levels they produce.

5.3 Stable Isotopes

A measurement of the stable isotopes $^{13}C/^{12}C$ (as $\delta^{13}C$) is included routinely in landfill gas measurements. Interpretation of all these results is discussed in a further section.

6 Notes on the Collection of Landfill Gas Samples for Carbon-14 and Tritium Measurements

Because of the quantities of methane required for the measurements, samples are best collected in plastic (15 litre) containers or similar sizes of TEFLAR sample bags. Metal Gresham tubes, even at pressure, do not in general provide the required quantities. Suitable containers can be loaned from RCD for the cost of postage and packing (a charge is made for the bags if they are not returned, however). A small 12v diaphragm pump may also be loaned but most operators prefer to fill the bags from the exit port of their methane detection equipment. In this way the methane concentration can be monitored continuously through the filling process. Care should be taken over this as the concentration in the gas may fall during the filling process. If feasible, the gas from the bag should be tested before recording the final methane concentration.

Filling time per bag may be of the order of 15 to 20 minutes but will take longer if a stop has to be made to allow the methane concentration to replenish.

Bags should be labeled with a unique location/time identification using the parcel labels supplied and returned to RCD with instructions of the tests required and any permitted variations, eg whether a second bag can be used if the first is inadequate.

6.1 Sample Requirements

Table 1 lists the practicalities of providing sufficient gas for measurement.

Table 1 Quantities of Gas Required

Measurement Method	Minimum Carbon Required	Absolute minimum volume of CH_4 Required		
		100%	10%	5%
Benzene Synthesis	1g	~2 litres	~15 litres	~30 litres
AMS	5mg	10 ml	100ml	200ml

For the in-house laboratory measurements (benzene synthesis followed by liquid scintillation counting – LSC) RCD require the sample provided to yield at least 1g carbon for the ^{14}C measurements and approximately 3g water for direct LSC determination of the ^{3}H content. Below this minimum amount, ^{3}H measurements are more difficult but for ^{14}C an alternative method using accelerator mass spectrometry (AMS) can be used. For this method RCD process the sample to CO_2, seal it in a glass vial and despatch it to an AMS laboratory, eg Groningen, The Netherlands, for the ^{14}C determination. The procedure is more expensive than the in-house method and there may be 6 to 8 weeks delay between despatch of the processed sample and the return of the measurement results. With the in-house method results are usually supplied within 3 to 6 weeks of receipt of the sample.

6.2 Measurement Procedure

6.2.1 Samples for CH_4 Analysis only

The supplied gas is drawn from the sampling bag through a soda lime column (to strip out any included CO_2) and a dried silica gel column to remove any water vapour. The residual stream is then passed over a Palladium based catalyst heated to ~450ºC to combust the CH_4 (and any other organic components) to CO_2 and H_2O. The H_2O (containing the tritium) from the methane is then collected cryogenically (dry ice trap cooled to -78ºC) and the CO_2, similarly collected in a liquid nitrogen trap (-196°C). The expanded CO_2 is then converted to C_6H_6 through the stages of lithium carbide and acetylene. In the case of very small samples the CO_2 is dispensed into and sealed in a glass vial for despatch to an AMS laboratory for the ^{14}C determination.

6.2.2 Samples for CO_2 and CH_4 Analysis

The procedure is basically the same as given in 2.1.1 above but the CO_2 gas absorbed in the initial soda lime column becomes the required sample. A measurement is then made of the CO_2 obtained by acidification of the soda lime to determine separately the ^{14}C content of the CO_2 component

6.2.3 Counting

For ^{14}C the produced C_6H_6 samples are dispensed for counting using butyl-pbd as scintillant and measured in a Wallac Quantulus liquid scintillation counter, optimised for low level counting, in association with both background and modern standards, the modern standard being NBS Oxalic acid, which is the primary international standard supplied to all Radiocarbon measurement laboratories. The samples are counted for 1000 minutes or the time to accumulate > 10,000 counts (1.0% counting statistics).

For ^{3}H an aliquot of the produced water samples is dispensed for counting of the tritium with a proprietary scintillant and similarly measured in a Wallac Quantulus in association with background and standard samples. The standard for the ^{3}H counting is primarily an IAEA supplied sample backed up by intercomparison with a diluted standard supplied by RCD Amersham in collaboration with Health Physics at the JET Facilities, UKAEA Culham. (RCD regularly takes part in any possible intercomparison with local laboratories and those organised internationally.) The samples are counted for either 500 minutes or the time to accumulate approximately 10,000 counts (1%

counting statistics). However, for both the tritium and the carbon-14 samples the error term given represents full replicate sample reproducibility and not counting statistics alone.

7.0 Note on Presentation of Landfill Gases' Results and Interpretation

7.1 Carbon-14

^{14}C activity is expressed as 'Percent Modern', 100% being the internationally agreed undisturbed level at which ^{14}C is naturally produced in the atmosphere. It is, in theory, the level which all organic material achieves during its life as a plant or animal. After death this level slowly diminishes by the radioactive decay process, to half its original value after 5730 years (Half Life).

Two situations have upset the theoretical ^{14}C in the atmosphere situation in recent years (demonstrated in Figure 1). Firstly, pre-1950, the level is slightly below 100% at ~98% and this is attributable to the dilution of CO_2 in the atmosphere by the combustion of fossil fuels (zero ^{14}C) since the onset of the industrial revolution. Secondly, beginning in 1950, the atmospheric level increased rapidly to a peak approximately twice the normal level by 1963. This was due to the atmospheric nuclear weapons' testing programmes which took place between 1950 and 1963. Since then the levels have slowly fallen to around 110% by 2000. This decrease was due to absorption of the CO_2 into the greater CO_2 reservoir of the oceans, not radioactive decay alone.

At RCD the measurement precision attained is of the order of ± 1% (standard deviation). This means that the lowest measurement that can be quoted with confidence as a positive value has to be greater than 3%.

On a practical point concerning the collection and processing of gas samples it is recognised that with the ambient level of air at ~110% non-contamination of a truly zero sample is sometimes difficult to achieve and may need further testing (by replicate sampling) to confirm values even up to 10%.

7.2 Tritium

Tritium measurements are expressed as Bq/l, the SI units for radioactivity specific activity measurements and/or in the ratio form favoured by many geologists and hydrologists, 'TU'. The TU presentation is independent of the quantity measured and refers to the ratio of the nonradioactive to radioactive atoms present in whatever organic or inorganic species in which it occurs. By definition 1 TU is a ratio of 1 atom of Tritium to 10^{18} atoms of protium (hydrogen).

Like ^{14}C, ^{3}H also occurs naturally in our atmosphere and produces a level estimated to be around 0.2 Bq/l (~2 TU). During the thermonuclear weapons trials of the 1950s to 1960s these levels increased several hundredfold and produced identifiable peak levels in soil moisture. Since then, however, through dilution and radioactive decay (half-life 12.43 years) these elevated levels are barely discernible in groundwater or soil moisture, the current precipitation levels being only of the order of 1 to 3 Bq/l (~30 TU maximum).

In landfill gases, tritium is measured by direct counting of the water produced in the oxidation of the CH_4 content. A minimum of around 1g H_2O is required to obtain a measurement precision of ± 1 Bq/l (~10 TU), which corresponds to a theoretical least measurable level of ~3 Bq/l (~30 TU). Samples giving greater than, say 110 Bq/l are suspected of containing a small higher level component. Much higher levels (factor of x1000 higher) are frequently found in CH_4 from waste sites in which artificially produced ^{3}H has been deposited. ^{3}H extensively used in the late 1960s to 1970s to enhance the luminosity of such items as clock and watch dials, objects which eventually turned up in landfill sites and, by methanogenesis, into CH_4.

7.3 Stable Isotope Ratio ($\delta^{13}C$)

$\delta^{13}C$ is the third isotope measurement reported in the landfill gas results and is expressed in terms of a difference (‰) in the $^{13}C/^{12}C$ ratio value of the gas compared with that in an internationally agreed standard. Negative values indicate a depletion in the relative ^{13}C content of the sample compared with that of the standard. $\delta^{13}C$ values range between around + 2‰ in natural geological materials (eg rock carbonate) to around -70‰ in biogenically produced CH_4, such as found in a typical landfill gas CH_4. $\delta^{13}C$ values of organic material, eg most terrestrial plants and trees, however, are around -25‰ with generally less than ± 5% variation from species to species (except for some C3 plants, not common in the UK, which centre around -12‰). In contrast biogenic CH_4 sources show wide variation sometimes in excess of ± 30% of the values given above.

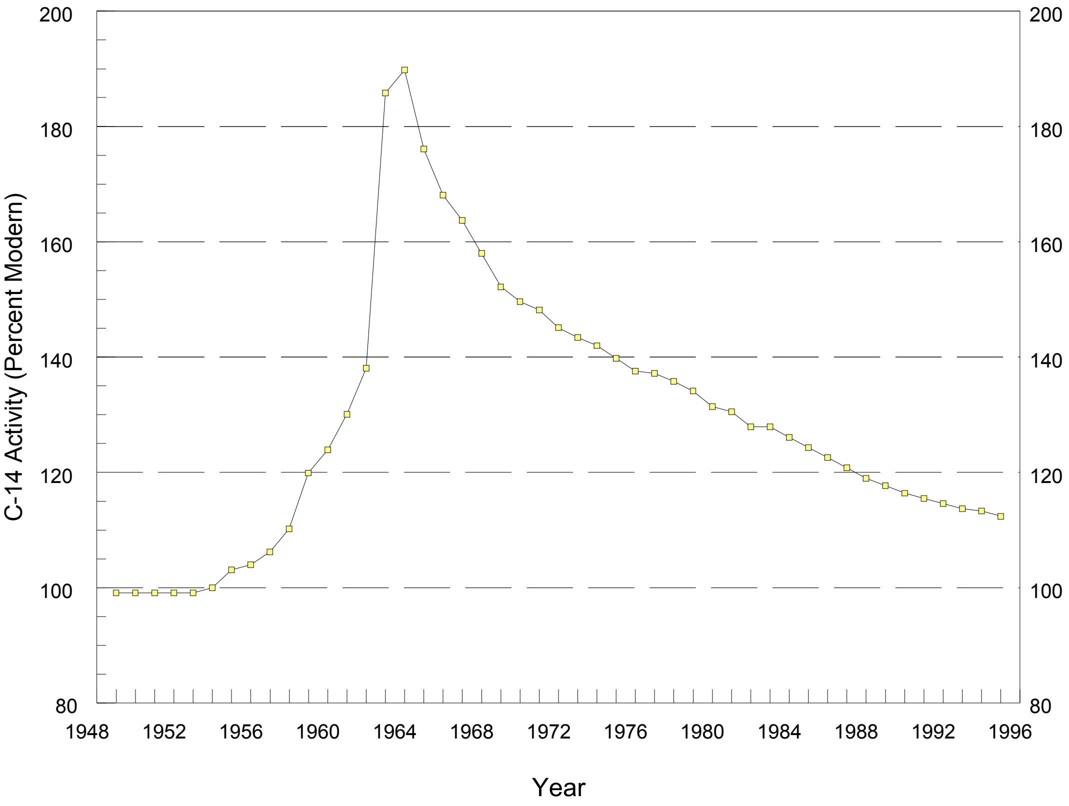

Figure 1 Carbon-14 in UK Natural Materials, 1948 to 1996

APPENDIX I

PRICE LIST

Prices on application

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