
Chapter Two

*The Importance of
Stable Isotopic Determination
of Methane*

2.1 Introduction - *Why Study The Isotopic Composition of CH₄?*

Chapter One describes the importance of CH₄ as a greenhouse gas, and its key role in atmospheric chemistry. This chapter will concentrate on the importance of measuring the isotopic composition of CH₄. The study of the isotopic ratios of CH₄ emitted from different sources provides useful information about the sources and their effect on the global CH₄ cycle (Stevens *et al.*, 1988; Wahlen, 1994). Isotopes studied in this thesis are ¹²C, ¹³C, ¹H, and ²H.

2.1.1. Carbon and Hydrogen Isotopes

Isotopes of a particular element have the same number of nuclear protons but differing numbers of neutrons. The isotopes of an element, although essentially the same, will show physical and chemical differences. The key isotopes involved in the study of CH₄ are shown in Table 2.1.

Although Table 2.1 lists carbon-14, it is not a target for this research, although a brief description of its use is given in this chapter.

Name	Symbol	Stable or Radioactive	Abundance (%)/ Half-life
CARBON			
Carbon – 12	¹² C (carbon)	Stable	98.90
Carbon – 13	¹³ C	Stable	1.10
Carbon – 14	¹⁴ C (radiocarbon)	Radioactive	5730 years
HYDROGEN			
Hydrogen – 1	¹ H (hydrogen)	Stable	99.985
Hydrogen – 2	² H (deuterium)	Stable	0.015

Table 2.1 – A summary of the carbon and hydrogen isotopes used to investigate CH₄.

Isotopes of an element are measured as ratios of each other by a mass spectrometer. There are two specific types of isotope: stable and radioactive. It is the stable isotopes of H and C that are commonly used for the study of CH₄. The carbon

ratio $^{13}\text{C}/^{12}\text{C}$ and $^2\text{H}/^1\text{H}$ (D/H) are the most commonly measured. Radiocarbon or ^{14}C has been studied (Wahlen *et al.*, 1989b; Kunz, 1985) to assess the contribution of fossil CH_4 to the global budget, as fossil CH_4 contains no ^{14}C in comparison with the modern quantities of ^{14}C in biogenic CH_4 in the atmosphere. This fossil CH_4 is generated during gas exploration, natural gas seepages and coal mining. ^{14}C in CH_4 is measured using an accelerator mass spectrometer, which has yielded a value of approximately 120 pMC (percent modern carbon) (Tyler, 1991). Unfortunately this research is complicated in the northern hemisphere by emissions of $^{14}\text{CH}_4$ from nuclear reactors (Eisma *et al.*, 1994), and is best carried out in the high southern latitudes.

2.1.2 Stable Isotopic Notation

Stable isotopes are represented in the δ -notation as ratio values. This value is measured on a mass spectrometer and is quoted as a deviation from a known standard ratio. Internationally the standard reference for C is Pee Dee Belemnite (Craig 1957) or PDB, and for H, Vienna Standard Mean Ocean Water (VSMOW) (Hagemann *et al.*, 1970). The ratios are quoted as a per-mil (‰) deviation from the reference. If a sample contains higher quantities of the heavier isotope (e.g. ^{13}C for carbon) it is enriched (or colloquially, heavy) and vice-versa, if the sample contains more of the lighter isotope (e.g. ^{12}C for carbon) it is depleted (or 'light').

2.2 The Use of Stable Isotopic Ratios in the Determination of CH_4 sources.

Although C and H isotopes have essentially the same atomic structure, the difference in mass can affect the chemical behaviour of CH_4 molecules. Measurements of $^{13}\text{C}/^{12}\text{C}$ and D/H in individual molecules of CH_4 can be used to determine the different isotope fractionation with respect to the initial C and H pools used for the resulting CH_4 . These are clearly distinguishable for the three principal CH_4 production processes:

1. **Biogenic (microbial) CH_4 formation via acetic fermentation.** This occurs in anaerobic environments, such as areas of stagnant H_2O coverage (i.e. rice paddies, beaver ponds etc.) or areas where anaerobic conditions are

dominant (i.e. landfill sites) and alimentary canals of animals. Methanogens are Archaea, and characteristically produce CH₄ showing strong depletion in ¹³C (Oremland *et al.*, 1987; Hanson, 1980; Rudd and Taylor 1980).

2. **Thermogenic formation** such as natural gas generation. Natural gas can form both inorganically or by microbial processes and different sources of natural gas can be determined by stable isotopic ratio determination of the CH₄. Natural gas from the North Sea for example is thermogenically generated and the CH₄ derived has a δ¹³C value of approximately –33‰ (Lowry, unpublished data). This is in contrast to some of the gas generated in Siberia by microbial pathways, which has a range of δ¹³C values between –48 and –65‰ (see Grace and Hart, 1986). This microbially derived natural gas is more depleted in ¹³C than thermogenically produced natural gas.
3. **Incomplete combustion** of biomass or fossil fuels (see chapter 7), producing CH₄ relatively enriched in ¹³C.

The isotopic ratios of CH₄ can be changed during the above processes by 2 main chemical and physical processes:

- **Kinetic Processes**, e.g. bacterial reactions. The lighter isotopes of CH₄ (¹²C and ¹H) are preferentially involved in chemical reactions as they require lower activation energy to achieve the physical changes within the molecule (i.e. bond breaking), necessary for chemical reactions to occur.
- **Isotopic exchange**, this occurs between different chemical substances, phases or individual molecules in an attempt to achieve isotopic equilibrium; this includes thermal isotopic equilibrium.

This imprinting of an isotopic signature by these two methods can help to define an isotopic signature of the source of a CH₄ molecule.

The amount of ¹³C and D in CH₄ from clean air samples, which globally, only varies slightly between different locations, (see Figures 2.1 and 2.2), can be compared with the amount present in individual sources. The results of such comparisons can be

used to make estimates of the relative source strengths of CH₄. In addition, ¹³C/¹²C and ²H/¹H ratios help ascertain the sources of increments of CH₄ to the atmosphere. Stevens and Rust (1982) originally proposed that the mass-weighted average composition of all the sources of CH₄ should equal the mean δ¹³C of atmospheric CH₄ corrected for any fractionation effects in the CH₄ sink reactions (e.g. removal by •OH).

2.3 Stable Carbon Isotopes in CH₄

The stable carbon isotopic ratio of CH₄ in atmosphere is in the region of -47‰ (for examples see; Lowe *et al.*, 1994; Lowry *et al.*, 1998; Tyler *et al.*, 1999; Quay *et al.*, 1999). This is depleted with respect to organic carbon mainly as a result of the CH₄ source mix, which is dominated by methanogenesis. This depletion occurs by isotopic fractionation during carbon degradation and in microbial CH₄ production. The δ¹³C of atmospheric CH₄ is also fractionated during removal by the •OH radical, the largest atmospheric sink of CH₄. Cantrell *et al.* (1990); Saueressig *et al.* (1995); and Gupta *et al.* (1997) have studied the fractionation effect caused during removal by •OH, it is estimated at approximately -5.4‰. Aerobic CH₄ consumption by dry soils is a secondary global sink of CH₄ of 1-10% (Born *et al.*, 1989). The isotopic fractionation by soils has been measured at between 25-29‰ (King *et al.*, 1989) and must be taken into account when calculating global isotopic budgets.

Biogenic CH₄ is variably depleted in ¹³C with respect to the carbon source. Rust (1981) found that CH₄ from ruminants differed in δ¹³CH₄ according to the food they ate (C₃ versus C₄ feed plants), indicating that the isotopic composition of ruminant CH₄ is dependent on the isotopic ratios of substrate carbon and the impact of methanogenic pathways (Wolin and Miller, 1987). Biogenic CH₄ from wet, anaerobic environments (wetlands, rice paddies and tundra) is also depleted with respect to ¹³C (Quay *et al.*, 1988).

Major sources of CH₄ generated by non-methanogenic processes include natural gas and biomass burning which are thermogenic in origin. These have a δ¹³C signature that is isotopically heavy compared with microbially produced CH₄.

The measurement of $\delta^{13}\text{C}$ of CH_4 has been more common than δD . This has been due mainly to the difficulty of analysing CH_4 for hydrogen isotopes. The main reason for the development of the new cryogenic line at RHUL is to allow analysis of δD of CH_4 in relatively small atmospheric samples.

The variety of isotopically distinct pathways outlined above, suggests that sources of CH_4 can be distinguished by the study of $\delta^{13}\text{C}$. However, to distinguish some of the methanogenic reaction pathways, especially at different latitudes, the investigation of the D/H ratios in the evolved CH_4 is needed.

2.4 Stable Hydrogen Isotopes in CH_4

There is a interhemispheric difference of δD of $\sim 10\%$, with the southern hemisphere being heavier than the northern hemisphere (Wahlen 1990). This is thought to represent different δD source mixtures for the two hemispheres, caused perhaps by more biomass burning CH_4 (enriched in δD) in the southern hemisphere (see chapter 7), and more depleted biogenic CH_4 from the northern hemisphere, where both land distribution and population are more abundant. δD of biogenically produced CH_4 is highly depleted due to a large fractionation effects (see Figure 2.3).

Although measured by few laboratories, δD of CH_4 is well suited to distinguish between different methanogenic pathways and environments that are major sources of CH_4 in the atmosphere. In contrast to carbon isotopic ratios of CH_4 , the H isotope data for CH_4 do not exhibit a clear dependency on maturity or oxidation effects; rather, they provide details on depositional environment and chemical pathway during formation. Hydrogen isotopes are particularly useful in distinguishing:

1. CH_4 from different methanogenic pathways
2. Bacterial from early mature thermogenic gas
3. Thermogenic from geothermal-hydrothermal gas
4. Latitudinal variation of sources.

In these examples the C isotopic ratios of CH_4 , if used alone, would deliver ambiguous results (Whiticar, 1993).

The δD of CH_4 produced in an inundated ecosystem (e.g. peat bogs, paddies, and tundra) shows a strong correlation with the δD of the local precipitation. The number of H atoms, derived from meteoric H_2O and incorporated into CH_4 produced by microbes in these conditions, is different during acetate fermentation and CO_2 reduction pathways. Thus, for the isotopic signature of precipitation to carry through consistently into that of the CH_4 produced, it is necessary that the pathway mix (acetate fermentation versus CO_2 reduction) is fairly constant in these diverse ecosystems (Wahlen, 1994).

The quality of the data obtained worldwide should be consistent as the determination of both C and H stable isotopic signatures in CH_4 is important. The next section of this chapter will discuss the factors that must be considered when discussing data quality.

2.5 Data Quality

There are two main aspects of concern when assessing the quality of data: i) the accuracy, and ii) reproducibility of the figures measured. The accuracy or truth, of numbers can be determined by calibration and intercalibration between laboratories and standards agencies. This needs to be of adequate quality so that the results obtained can be compared. The second factor which is more important to a single laboratory study is the reproducibility of data. Reproducibility of a result is the range of figures obtained for repeated analysis of one sample. The range of results measured for CH_4 , and the resolution required to determine changes or differences within these results dictates the required precision. This section outlines the required precision for measurement of stable isotopes in CH_4 .

2.5.1 Carbon

The required precision of carbon isotopic results are entirely dependent on the range of $^{13}C/^{12}C$ in CH_4 that need to be distinguished. This can be split into two categories: analysis of air containing background quantities of CH_4 , and air used for source identification and signature investigation. The precision required for the determination of $^{13}C/^{12}C$ of CH_4 in background air is dictated by the seasonality of carbon isotopes. At RHUL a carbon isotopic record has been maintained using air

masses from the Atlantic, collected at Mace Head, on the west coast of Ireland. The samples have been analysed on the NIWA style cryogenic extraction line and the results are shown in Figure 2.1. Other laboratories have also monitored the background isotopic composition of CH₄ with respect to C (for examples see Levin *et al.*, 1997; Lowe *et al.*, 1998) and achieve similar seasonality. Figure 2.1 shows the isotopic seasonality of clean background air with respect to $\delta^{13}\text{C}$ in CH₄ for sites in both the northern and southern hemisphere.

The seasonality of the curves in Figure 2.1 is less than 0.8‰, and therefore to accurately measure and ascertain a pattern of seasonality with confidence the reproducibility of the stable isotopic numbers of carbon in CH₄ must be better than 0.05‰. To determine carbon isotopic ratios of CH₄ that has been derived directly from a source and therefore is concentrated, the required precision can be reduced by an order of magnitude as the difference in isotopic ratio between classes of individual sources is large enough to ensure that 0.5‰ is adequate to differentiate between each source type, once the sources have been characterised.

2.5.2 Hydrogen

The measurement of ²H/¹H (D/H) ratios in CH₄ is not common in the literature or the CH₄ community. It is the primary reason for the development of the new line at RHUL. Some D/H ratios of atmospheric CH₄ have been measured. Wahlen *et al.*, 1987, 1989a; Levin *et al.*, 1997; Bergamaschi, pers. comm.) have measured air samples to determine D/H ratios in background atmospheric samples of CH₄. Figure 2.2 shows 2 plots of D/H seasonality in background quantities of CH₄. The seasonality is synchronous with carbon (Levin *et al.*, 1997) and exhibits larger seasonal amplitudes (approximately 5-10‰) than $\delta^{13}\text{C}$. Thus the precision required to measure atmospheric seasonality is less than for C. However it should be noted that the maximum precision possible should be sought from a technique of measurement.

Figure 2.1

Figure

2.2

2.6 Measurement Techniques

This section documents the precision of measurements of various techniques used to generate the isotopic information of CH₄. There are two main types of technique used to measure the stable isotopic composition of CH₄. Some techniques are only designed for the determination of ¹³C/¹²C ratios; others are designed to analyse both ¹³C/¹²C and ²H/¹H. These methods are i) chemical preparation of air samples for isotopic analysis and, ii) direct measurement of sample gas. The two main factors that are very important when assessing the methods for stable isotopic analysis of CH₄ are the size and concentration of the air sample required for a component isotopic analysis and secondly, the precision of the measurements obtained by that quantity of air sample. It would appear from the literature that the measurement of carbon isotopic compositions of CH₄ was historically chosen for development as it was easier to obtain better precision than δD, and analysis of CO₂ is far more straightforward than H₂. Techniques for the determination of H isotopes were developed secondarily: δD determination of CH₄ is necessary to distinguish between some sources that are not separated by δ¹³C.

2.6.1 Direct Measurement of Isotopes in CH₄.

The techniques that have been classed ‘direct’ do not involve conversion of CH₄ to H₂O and CO₂ for measurement on a conventional isotope ratio mass spectrometer (IRMS). There are two main methods of direct measurement of carbon and hydrogen isotopes in CH₄:

2.6.1.1 Tuneable Diode Laser Techniques

This technique described by Bergamaschi *et al.*, (1994), utilises the differential vibrational transitions and the corresponding infrared spectra for the different CH₄ isotopomers to determine δ¹³C and δ²H measurements on CH₄ gas. A Tuneable Pb-salt diode laser is tuned to the spectral regions of the retrospective absorption pairs (C and H). The laser beam is split into two beams of light, one of which is passed through a multi-reflector cell, and the other through a reference gas of known isotopic composition. This technique can analyse both

background and concentrated source samples e.g. landfill gas (Bergamaschi *et al.*, 1995) to a precision of $\pm 0.44\%$ for $\delta^{13}\text{C}$ and 5.1% for δD . The quantity of gas or concentration required for such an analysis is documented as 50ppm for carbon isotopic ratio determination and 2000ppm for D/H analysis. Therefore to complete analysis on background quality air with a low CH_4 content ($\sim 2\text{ppm}$) requires the pre-concentration of an air sample. This is not necessary for the analysis of source samples, which are usually concentrated due to the proximity of sampling to the source.

2.6.1.2 Static Mass Spectrometry to Measure $\delta^{17}\text{M}$

This technique was developed at the Planetary Sciences Research Institute, The Open University, Milton Keynes in the United Kingdom and is described in Morse *et al.* (1996), Jackson *et al.* (1999). The method uses a static mass spectrometer coupled to a gas chromatograph, and uses CH_4 as an analyte to determine a combined $\delta^{17}\text{M}$ figure (δD and ^{13}C simultaneously). This method can measure small air samples (10ml) of ambient air, and produce $\delta^{17}\text{M}$ values with a precision of 0.26% . The back calculation required to determine the $\delta^{13}\text{C}$ and δD of the CH_4 in a sample requires a conventional measurement of one of the isotopes in order to calculate the other. The measurement of $\delta^{13}\text{C}$ and δD must therefore adhere to the restrictions of all the techniques described in this section. Therefore, the quoted precision for $\delta^{17}\text{M}$ is reliant on the precision of another technique for calculation of the $\delta^{13}\text{C}$ and δD content of an air sample.

2.6.2 Chemical Preparation of CH_4 for Isotopic Analysis

All the techniques described below are variations upon a theme. The techniques involve the preparation of CH_4 by cryogenic extraction or pre-concentration for combustion in excess oxygen to form either/or CO_2 and H_2O for isotopic measurement of $\delta^{13}\text{C}$ and δD respectively. A number of these techniques have been established worldwide for the stable isotopic determination of CH_4 . An important factor to consider is the design of the technique with respect to the concentration of CH_4 that will be processed. Generally these samples are either i) atmospheric air samples with a low CH_4 concentration (1800-4000 ppb) or ii) CH_4 collected from a source location with

typically a higher concentration of CH₄. Some of the techniques are designed for δ¹³C analysis only, but others can process CH₄ for δ¹³C and δD analysis.

2.6.2.1 Reaction of CH₄ at Atmospheric Concentration Levels

The first apparatus specifically for the preparation of atmospheric quantities of CH₄ was designed by Lowe *et al.*, (1991). This type of 'NIWA' line is already installed at RHUL for δ¹³C analysis of CH₄. The technique involves the passage of an air sample at a known rate through glass traps. The line uses liquid nitrogen to cool these traps to condense components of the air such as H₂O and CO₂. A trap filled with Schütze reagent (Iodine Pentoxide on silica gel, I₂O₅) is used to convert CO to CO₂ for subsequent removal from the airflow using a trap cooled with liquid nitrogen. After extraction of CO₂ and CO the air sample in the line contains no significant carbon species other than CH₄, which is then combusted on platinised alumina pellets at 750°C to produce CO₂. The CO₂ is then collected in a series of traps at liquid nitrogen temperature. The CO₂ can then be thermally distilled and collected for analysis on an IRMS. The size of atmospheric sample required for this type of analysis including flushing is approximately 90L. The precision of this technique originally published in 1991 was 0.1‰, but has now been refined to 0.05‰ by NIWA in New Zealand (Lowe *et al.*, 1998) and at RHUL in the Atmospheric Monitoring and Isotope laboratory to 0.03‰ on duplicate samples of 90L and 0.05‰ on secondary standards run bi-weekly over a 2-year period (Lowry *et al.*, 1998). This technique was designed to produce gas for the analysis of δ¹³C in atmospheric samples of CH₄; it cannot process high concentration samples, or give good yield of H₂O for δD analysis because of the sponge like H₂O retention of the catalyst media.

The new line at RHUL constructed for this thesis is based on this line, but designed to remove atmospheric H₂ from an air sample thus enabling the preparation of air for δD determination of CH₄.

2.6.2.2 Analysis of Concentrated Samples (including pre-concentration techniques)

Pre-concentration of CH₄ in gas samples is used when the level of CH₄ is too low in the sample size for the chosen technique to operate efficiently. A number of methods have been established for the analysis of CH₄, which utilise a variety of chemicals to act as either a catalyst for the oxidation of CH₄ or utilise a direct redox reaction to produce CO₂ and H₂O. All of these techniques combust CH₄ for dual-stable isotopic analysis. Pre-concentration is adaptable as techniques can analyse a variety of CH₄ concentrations.

Each of these methods are outlined below:

A technique used at Institut für Umweltphysik (IUP-Heidelberg) (Levin *et al.*, 1993) pre-concentrates atmospheric CH₄ samples in a two-stage process. Initially the sample is absorbed onto activated charcoal at -196°C. After desorption from the charcoal at 300°C, the sample is purified using a preparative gas chromatograph. This pure CH₄ is then combusted with synthetic air to produce CO₂ and H₂O in a closed circuit system using a platinum catalyst at 900°C. H₂O and CO₂ are trapped at -78°C and -196°C respectively. The volume of sample required for a single isotopic analysis is 600-800L for CH₄ at atmospheric levels. More concentrated samples can be smaller. The precision on the isotopic ratios achieved on this line is quoted as ±0.05‰ for δ¹³C (Levin *et al.*, 1999), and ±5‰ for δD (Levin *et al.*, 1993).

A variation of the technique used at IUP-Heidelberg is used at University of Washington, Seattle. Quay *et al.*, (1991, 1999), and originally Stevens and Rust, (1982), describe a method for the preparation of CH₄ for both atmospheric and concentrated sample analysis for carbon ratio determination. The air sample is metered through a high vacuum line through a series of liquid nitrogen temperature glass traps that remove CO₂ and H₂O. A trap filled with Schütze reagent is used to convert CO to CO₂, which is subsequently removed by a trap at -195°C. The remaining air stream is passed through an oven containing platinised silica at ~800°C which oxidises CH₄ to CO₂. This CO₂ is collected in a liquid nitrogen trap. The catalyst is purged with helium or zero

air to reduce sample memory on the catalyst. Approximately 15 to 30 litres of air containing atmospheric levels of CH₄ are used for sample preparation and the technique can achieve a reproducibility of $\pm 0.1\text{‰}$ for $\delta^{13}\text{C}$ (Quay *et al.*, 1999). The method used at the University of Washington for D/H analysis of atmospheric CH₄ involves the pre-concentration of 100L of air sample on activated charcoal at -195°C . This is subsequently desorbed at 100°C and reacted on platinised quartz wool at a temperature of 730°C . The CO₂ and H₂O are cryogenically collected in a Pyrex U-shaped tube and the CO₂ is transferred away at -80°C . The H₂O is analysed after reduction to produce a claimed δD reproducibility of 2‰ and 0.09‰ for $\delta^{13}\text{C}$.

The final two methods summarised in this chapter do not use a catalyst to initiate the oxidation of CH₄. The oxidation is facilitated by copper II oxide (CuO or cupric oxide). The drawback of using this technique is that the oxidant is finite and therefore must be replaced when spent.

The first of these methods is designed specifically for the preparation of concentrated source samples. The technique described by Hitchman *et al.* (1989), utilises a nitrogen gas purge to introduce the sample to a reaction chamber filled with CuO at 800°C . The sample gas passes through an ammoniacal barium chloride to precipitate CO₂. A 'drierite' trap is used to remove any non CH₄-H₂O prior to reaction with the CuO. The resulting CO₂ and H₂O from the combustion of CH₄ are cryogenically trapped and the CO₂ and H₂O are separated for isotopic analysis. This technique has no quoted sample size requirement or precision for the isotopic analysis.

The second method that uses CuO as an oxidising agent for CH₄ was developed by Revesz *et al.* (1995). The technique uses two methods, one for low and another for more concentrated samples. Samples that contain between 1ppm and 5% CH₄ require pre-concentration on activated charcoal at -195°C , which absorbs the CH₄. This is then purified by gas chromatography and oxidised by Cu at 450°C and CuO at 800°C . The number of steps is reduced for samples containing between 5 and 20% volume of CH₄ as the initial pre-concentration on charcoal is omitted. Samples that contain 100% CH₄ and no other C or H contamination are combusted directly in the Cu based furnaces.

The reproducibility of these techniques is $\pm 0.13\%$ for $\delta^{13}\text{C}$ and ± 1.55 for δD (Revesz *et al.*, 1995), but the quantity of gas required is not outlined.

The techniques that require a chemical preparation to produce CO_2 and H_2O from CH_4 (catalytic and redox reaction) are limited by the minimum quantities of CO_2 and H_2 required for competent stable isotopic analysis. Therefore a balance must be achieved between sample size and concentration. The methods described in this section are summarised in Table 2.2.

Direct/ Chemical Conversion	Pre- conc. Needed	Oxidation Chemical	Sample Size (L)	Ideal CH_4 Conc. (ppm)	Quoted Precision (‰)		Reference
					$\delta^{13}\text{C}$	$\delta^2\text{H}$	
DIRECT	Y	N/A	Adequate to obtain conc. required	50ppm ($\delta^{13}\text{C}$) 2000ppm ($\delta^2\text{H}$)	0.44	5.1	Bergamaschi <i>et al.</i> , 1995
DIRECT	?	N/A	10 ml for $\delta^{17}\text{M}$ analysis	?	0.26‰ for $\delta^{17}\text{M}$		Morse <i>et al.</i> , 1996 Jackson <i>et al.</i> , 1999
CHEMICAL	N	Pt on Alumina	90	Atmospheric levels	0.05	Incapable of D/H analysis	Lowe <i>et al.</i> , 1991 Lowry <i>et al.</i> , 1998
CHEMICAL	N	Pt on quartz Wool	100	Atmospheric and Source	See below	4	Quay <i>et al.</i> , 1999
CHEMICAL	N	Pt on Alumina	30	Atmospheric	0.1	See above	
CHEMICAL	Y	Pt	600-800	Atmospheric levels	0.05	5.0	Levin <i>et al.</i> , 1993
CHEMICAL	N	CuO	?	Source Concentration	?	?	Hitchman <i>et al.</i> , 1989
CHEMICAL	Y	CuO	?	1ppm-5%	0.13	1.55	Revesz <i>et al.</i> , 1995
CHEMICAL	N	CuO	?	5%-20%	0.13	1.55	Revesz <i>et al.</i> , 1995
CHEMICAL	N	CuO	?	100%	0.13	1.55	Revesz <i>et al.</i> , 1995

Table 2.2 – A summary of techniques used to determine the stable isotopic composition of CH_4 .

2.7 CH_4 Stable Isotopic Variations

Figure 2.3 has been constructed to illustrate the importance of the measurement of both C and H isotopic ratios in CH_4 . It clearly shows that a combination of both $\delta^{13}\text{C}$

and δD data are required to distinguish all sources of CH_4 from each other. Many of the sources annotated in Figure 2.3 show varying carbon and hydrogen isotopic signatures, but many overlap in only one isotopic dimension. Samples from different ecosystems in waterlogged environments can be isotopically distinguished (rice fields, peat bogs, bogs and tundra), with only δD data for the methane.

At present, there is less information known about δD of atmospheric CH_4 than $\delta^{13}\text{C}$, but some data is available (for example: Ehhalt, 1973, Wahlen *et al.*, 1987). Based on recent studies, the δD of clean background air is between -67 and -115‰ with respect to standard mean ocean water (SMOW) (Levin *et al.*, 1997; Bergamaschi, 1999, pers. comm.), but the trend is toward enrichment in δD .

Figure 2.3 is a summary of some published δD and $\delta^{13}\text{C}$ ranges for all sources. The results published are varied and show huge ranges for various sources. It is clear that it is important not only to investigate the D/H numbers produced from the CH_4 source, but also to inspect more closely the conditions that are forming the CH_4 gas. For example, δD of landfill CH_4 is affected by the types of waste buried, temperature of the landfill, degree of oxidation and degree of bacterial degradation present (Ward *et al.*, 1996). A case study on biomass burning within this thesis has been designed to test the importance of vegetation type and moisture content in the resultant $\delta^{13}\text{C}$ and δD of CH_4 emitted to the atmosphere.

Intercalibration with as many laboratories as possible will be needed to develop a globally useful database, although this was beyond the scope of this research project. As a large proportion of the literature is based on the comparison of results, these can only truly be accurate if intercalibration is sought, and offsets between techniques and laboratories are understood.

2.8 Conclusion

In conclusion, the study of stable isotopic composition (both $\delta^{13}\text{C}$ and δD) of CH_4 is important as it can help determine global sources and their strengths. Isotopic data from the study of CH_4 can be used to determine source groups based on the pathway of CH_4 production. Work with hydrogen isotopes is needed to allow more

Figure 2.3

precise determination of some methanogenic sources which form up to 70% of the overall CH₄ emissions (Wahlen, 1994), and therefore it is imperative to increase the resolution of δD of sources.

The accuracy, precision and intercalibration of the stable isotopic measurements of CH₄ must be good, as background seasonality of both δ¹³C and δD is small, and to determine trends in this background air, precise isotopic ratios must be measured in CH₄. As yet the techniques for δD analyses require large amounts of CH₄ to be converted and do not have high precision. The design and construction of the new cryogenic extraction line at RHUL for this thesis was undertaken primarily to develop a new technique for the analysis of δD in CH₄ from atmospheric air samples, reducing the sample size requirements of previous techniques and with a precision significantly better than ±5%.