The ancestor of every action is a thought

Ralph Waldo Emerson (1803 - 1882)
This Master thesis has been performed at the Centre for Isotope Research (CIO) of the University of Groningen and represents the very first steps in my scientific career. The goal of this study was to install and improve an experimental set-up, capable of measuring the concentrations of Carbon Dioxide (CO$_2$), Methane (CH$_4$), Nitrous Oxide (N$_2$O), and Sulphur Hexafluoride (SF$_6$) in ambient air. The ability of measuring Carbon Monoxide (CO) was later added to the setup. This experimental setup will be used during my PhD study, to gain more insight in the effects of these anthropogenic greenhouse gases and trace gases on global climate, their sources and sinks and their regional distributions.

I would very much like to thank my supervisor Rolf Neubert for guiding me during this research. I consider it a privilege having him as my mentor during this project. Furthermore, I would like to thank Jan Schut for programming the Delphi-software that was used during this research, and supplying me with a control unit for the mass flow controllers. Thanks to Bert Kers, Henk Been and Henk Jansen for helping out with numerous of things, Anne Jelle Schilstra for reading the concept report and all of the other staff members (in particularly the PhD students) for their usefull ideas and comments during the coffee breaks.

Also, I would like to show my gratitude to our colleges from ECN (Cabauw). Their assistances in the beginning of my research are greatly appreciated.

Finally, I owe my thanks to Ingrid Luijkx for reading the first concepts of the thesis and her useful comments and ideas.

Sander van der Laan
Groningen, 30 July 2005
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The release of anthropogenic greenhouse gases into the earth’s atmosphere is by far the largest uncontrolled experiment in the history of the earth. Mankind is drastically modifying the composition of the atmosphere, both in greenhouse gases and aerosols. The consequences, especially for the long term, cannot be foreseen. The most important well-mixed greenhouse gases emitted by mankind are Carbon Dioxide (CO₂), Methane (CH₄) and Nitrous Oxide (N₂O). The present concentrations have not been exceeded for many thousands of years. Sulphur hexafluoride (SF₆) is a new, and highly stable atmospheric trace gas produced almost entirely by mankind. The greenhouse effect of SF₆ (on a per molecule basis) is one of the highest of any atmospheric greenhouse gases and it has an atmospheric lifetime of about 3200 years. When doing atmospheric greenhouse gas studies, their origin (fossil, oceanic, and terrestrial) can be determined by using tracers, for example SF₆ and Carbon Monoxide (CO). To gain more insight in the concentrations and distributions of these gases, a new measurement setup has been developed for in-situ measurements at Lutjewad, in the north of The Netherlands. The main component in this experimental setup is an Agilent HP 6890N gas chromatograph (GC) that is used to determine these greenhouse and trace gases both in a quantitative, and qualitative way. Measuring these gases in-situ and with high accuracy is one of the biggest challenges in atmospheric sciences. This report describes the adjustments that were made to the GC in order to make it possible to measure CO, and the improvements that were made in order to function with the required precision and accuracy. At the time of writing, we have no knowledge of any similar existing setup in the world. Thus, the possibility of measuring CO₂, CH₄, N₂O, SF₆ and CO with only one GC is probably unique. Besides having to purchase an expensive second device, the advantage of this method is that the different substances are measured on the same (sample) air, and under the exact same conditions, which make correlations between them more reliable.

The first test results indicate that the system experiences a significant drift. For this reason, the measurements of CO (± 15.8 ppb), N₂O (± 1.8 ppb) and SF₆ (± 0.5 ppt) are not yet within the desired accuracy of ± 1 ppb, ± 0.1 ppb and ± 0.1 ppt respectively. CO₂ (± 0.06 ppm) was measured with a standard deviation of almost the target (± 0.05 ppm) and CH₄ (± 1.46 ppb) is measured well within the target of ± 2 ppb. We must emphasize that these results are obtained from the very first test run with this new configuration, and fine-tuning of the setup, mostly the software related, has to be done to get better results. A calculation on data that was measured a few days later indicated already a significant improvement in the accuracy, and suggests that a large part of the inaccuracy of the measurements can still be attributed to start-up problems.

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1 Solid or liquid particles originating from either natural or anthropogenic sources. Typical sizes between 0.01 and 10 mm. Affecting climate by reflecting energy (both incoming and outgoing) and cloud formation.
2 The data of these measurements could not be included in this report.
SAMENVATTING

De uitstoot van antropogene broeikasgassen in de atmosfeer is zonder twijfel het grootste ongecontroleerde experiment in de geschiedenis van de aarde. De mensheid is drastisch bezig de samenstelling van de atmosfeer te veranderen, zowel qua broeikasgassen als aërosols\(^3\). De uitwerking hiervan, met name op de langere termijn, is niet te voorspellen. De belangrijkste broeikasgassen die uitgestoten worden door de mensheid zijn koolstofdioxide (CO\(_2\)), methaan (CH\(_4\)) en lachgas (N\(_2\)O). Hun hedendaagse concentraties zijn nooit overtroffen sinds ten minste vele duizenden jaren. Zwavelhexafluoride (SF\(_6\)) is een nieuw en bijzonder stabiel atmosferisch gas dat nagenoeg volledig door de mens wordt gemaakt. Het broeikaseffect van SF\(_6\) is, op molecule niveau, een van de hoogste van alle broeikasgassen, en het heeft een atmosferische levensduur van ongeveer 3200 jaar. Bij het onderzoeken van atmosferische broeikasgassen kan hun oorsprong worden bepaald aan de hand van zogenaamde spoorgassen (tracers), zoals SF\(_6\) en koolmonoxide (CO). Om meer inzicht te krijgen in de concentraties en verdeling van deze gassen word een nieuwe meetopstelling ontwikkeld in Lutjewad, Noord-Groningen. Het belangrijkste onderdeel van deze meetopstelling is een Agilent HP 6890N gaschromatograaf die gebruikt wordt voor de bepaling van de broeikas- en spoorgassen zowel op een kwalitatieve als op een kwantitatieve manier. Het meten van deze gassen met een dergelijke hoge nauwkeurigheid is momenteel een van de grootste uitdagingen van de wetenschap. Dit verslag beschrijft welke veranderingen er werden gedaan aan de GC om het goed te laten functioneren, en hoe het apparaat werd verbeterd zodat ook CO kan worden gemeten. Ten tijde van het schrijven van dit verslag was er geen vergelijkbare opstelling bekend elders in de wereld. De mogelijkheid om naast CO\(_2\), CH\(_4\), N\(_2\)O en SF\(_6\) ook CO te kunnen meten met één GC is dus waarschijnlijk uniek. Naast het niet te hoeven aanschaffen van een tweede, duur, apparaat, is een belangrijk voordeel dat alle verschillende gassen worden gemeten onder exact dezelfde omstandigheden en met één pakket monsterlucht waardoor er betrouwbare correlaties kunnen worden gemaakt.

De eerste testen wijzen uit dat het systeem nog onderhevig is aan een aanzienlijke drift. Dit is ook de reden dat de nauwkeurigheidseisen van respectievelijk ± 1 ppb, ± 0.1 ppb en ± 0.1 ppt, niet gehaald worden voor CO (± 15.8 ppb), N\(_2\)O (± 1.8 ppb) en SF\(_6\) (± 0.5 ppt). De nauwkeurigheid van CO\(_2\) (± 0.06 ppm) was nagenoeg hetzelfde als de ten doel gestelde maximale onzekerheid van ± 0.05 ppm, en de nauwkeurigheid van CH\(_4\) ± 1.46 ppb is zelfs hoger dan de gewenste nauwkeurigheid van ± 2 ppb. We dienen echter te benadrukken dat dit de allereerste testrun was met de nieuwe configuratie van de GC, en dat de set-up nog moet worden afgeregeld, voornamelijk de software, om betere resultaten te behalen. Een berekening aan de hand van data een paar dagen later gemeten\(^4\), wees uit dat de nauwkeurigheid al significant was toegenomen. Dit suggereert dat een groot deel van de onnauwkeurigheid kan worden toegericht aan opstartproblemen.

\(^3\) Vaste of vloeibare deeltjes van natuurlijke of antropogene oorsprong, typische grootte tussen 0,01 en 10 nm. Beïnvloedt klimaat door reflectie van energie (zowel inkomende als uitgaande energie) en wolkenvorming.

\(^4\) De data van deze metingen konden niet meer worden meegenomen in dit rapport.
Chapter 1: Introduction to the Research

This first chapter provides an introduction to the problem definition and the aim of this research. Also, some insights are given about the experimental setup that was developed during this research.

Human activities have increased the atmospheric concentrations of greenhouse gases and aerosols since the pre-industrial era. The atmospheric concentrations of the key anthropogenic greenhouse gases Carbon Dioxide (CO₂), Methane (CH₄), Nitrous Oxide (N₂O), and tropospheric Ozone (O₃) reached their highest recorded levels in the 1990s, primarily due to the combustion of fossil fuels, agriculture, and land-use changes (IPCC, 2001). Since 1750, the atmospheric concentration of carbon dioxide (CO₂) has increased by 31% and the present atmospheric CO₂ concentration (approx. 377 ppm) has not been exceeded during the past 420,000 years. Besides fossil fuel burning, another significant cause is changes in landuse, mainly deforestation. The atmospheric concentration of methane (CH₄) has increased by 1060 ppb since the year 1750. It has already increased for over 151% and continues to increase. More than half of the current CH₄ concentration (approx. 1800 ppb) is anthropogenic. Fossil fuel burning, cattle and agriculture are estimated to be the most dominant factors. Nitrous oxide (N₂O) has increased by about 46 ppb since 1750 to a current atmospheric level of 320 ppb. The present concentration has not been exceeded during at least several thousands of years (Houghton et al., 1992). About one third of the emissions are anthropogenic and can be attributed to agricultural soils, cattle feedlots and chemical industry. The radiative forcing due to the increases of the greenhouse gases from 1750 to 2000 is estimated to be in total 2.43 W/m², whereof 1.46 W/m² from CO₂, 0.48 W/m² from CH₄, 0.15 W/m² from N₂O (IPCC, 2001). Additionally some other emitted synthetic compounds (e.g. PerFluoroCarbons (PFCs) and Sulphur Hexafluoride (SF₆)) are also powerful greenhouse gases, and their concentrations are currently increasing. Sulphur hexafluoride (SF₆) is a highly stable atmospheric trace gas produced almost entirely by mankind. It is mostly used as electrical insulation and it is expected to have an atmospheric lifetime of about 3200 years (Maiss & Levin, 1994; Ravishankara et al., 1993). Its atmospheric concentration has increased by two orders of magnitude since 1970 (Lovelock, 1971) to a global mean value of about 2.8 ppt in 1992 (Maiss & Levin, 1994). The greenhouse effect of SF₆ (on a per molecule basis) is one of the highest of any atmospheric trace gases (Rinsland et al., 1990). When doing atmospheric trace gas studies, SF₆ can be used as a transport tracer (Maiss & Levin, 1994). To gain more insight in the concentrations and distributions of these gases, and to determine the vertical flux gradients on a regional scale, a new measurement setup is to be developed at Lutjewad (fig. 1.1), in the northern part of The Netherlands.

Figure 1.1: Left, the 60 meter high atmospheric monitoring station at Lutjewad. On the right, the location Lutjewad in the north of Groningen represented by the marked number on the map.

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5 Parts per billion: the ratio of the number of greenhouse gas molecules to the total number of molecules of (dry) air.
6 The change in balance between incoming and outgoing radiation in the top of the atmosphere.
7 Parts per trillion.
In short, the objective of this research is to:

*Develop an experimental setup* for use at Lutjewad, Groningen, capable of in-situ measurement of ambient atmospheric concentrations of the most important greenhouse gases and trace gases: CO$_2$, CH$_4$, N$_2$O, SF$_6$ and, if possible, CO$^\star$

The goal is to measure air samples from three different heights of the Lutjewad tower (fig. 1.2) semi-continuously with a gas chromatograph. This device is able to quantify CO$_2$, CH$_4$, N$_2$O and SF$_6$ at the same time. To further allocate the causes of observed variations in trace gases, an autosampler is installed so that certain air samples can be captured in flasks and examined for isotopic ratios. The flasks are each, one at a time, flushed for one hour (and then closed) with air samples. If no intervention from the operator takes place, the flask will be flushed again after 20 hours, with new air samples. Else, the flask stays closed and can be examined later in the laboratory. The choice of which air samples should be further examined, depends on whether or not an interesting event has occurred, such as for example a sudden increase in one of the trace gases. Therefore, the system has an online connection with a computer at the CIO. From here, the choice can be made to close a certain flask which contains an interesting air sample. Besides SF$_6$ and isotopic ratio measurements, further information about the origin of the air samples can be obtained by data from wind direction measurements (already installed) and $^{222}$Radon detection. The latter is obtained by using combined parallel observations of CO$_2$/CH$_4$, N$_2$O/SF$_6$ and $^{222}$Radon daughter activity as a semi-quantitative transport tracer.

The gas chromatograph (GC) is calibrated by measuring standard working gases several times per day. These working gases themselves are calibrated using high-pressure cylinder standard gases from the Climate Monitoring and Diagnostics Laboratory (CMDL) of the National Oceanic and Atmospheric Administration (NOAA), of Boulder (Colorado, USA), which is the international supplier of standard gases for atmospheric research. Calibration of the GC with the NOAA standards is done two times per year. The sample air is directed through a two-stage drying system consisting of a Nafton column$^8$ and a silicon oil based chiller trap with freeze fingers to remove the water from the air samples. Before any measurements take place at Lutjewad, the GC is first setup and programmed at CIO.

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$^\star$ Using an Agilent HP 6890N gas chromatograph

$^\star\star$ Added later to the research

$^8$ Membrane dryer used to remove water directly from the vapor phase.
CHAPTER 2: GREENHOUSE GASES AND TRACE GAS RESEARCH

The most important greenhouse gases, their origin and the effect on the global climate system are discussed in this chapter. First we will discuss the term ‘radiative forcing’ and its impact on the global average surface temperature. Next, we will briefly discuss the most important trace gases that will be measured with the gas chromatograph in Lutjewad in the Northern part of The Netherlands in order to provide some background theory about the subject.

2.1 Radiative forcing and greenhouse gases

Recent studies indicate that since 1861, the global average surface temperature has increased significantly, see figure 2.1. Most of this warming occurred during the 20th century, specifically during two periods: between 1910-1945, and 1976-2000. It is estimated (IPCC, 2001), that the total increase in average temperature during the 20th century has been 0.6 ± 0.2°C. This change in temperature has had already a significant effect on (especially regionally) the world’s food supply, droughts, spreading of diseases as malaria, increase in ocean levels and decreasing of snow cover and ice extent. More problems are expected for the remainder of the 21st century as global average surface temperature is estimated (with state of the art climate models) to increase even further with 1.4 to 5.8°C.

In principle, the average global temperature is a result from the energy the earth receives from the sun. The sun emits radiation at a temperature of about 5800 Kelvin, producing $3.9 \times 10^{23}$ kW in all directions. The result is that the annual amount of energy the earth receives is (on average) 342 W/m² (Boeker & van Grondelle, 1995). About 31% of this incoming radiation is reflected back into space by the earth’s albedo. A small part of the remaining radiation is absorbed by the atmosphere and most of it (168 W/m²) warms the earth’s surface. The atmosphere of the earth contains powerful, and natural, greenhouse gases that absorb radiation.

Figure 2.1: Combined annual land-surface air and sea surface temperature anomalies (°C) 1861 to 2000, relative to 1961 to 1990. The information is based on regular measurements of air temperature at land stations and on sea surface temperatures measured at ships and from buoys. Source: (Jones & Moberg, 2003)

In principle, the average global temperature is a result from the energy the earth receives from the sun. The sun emits radiation at a temperature of about 5800 Kelvin, producing $3.9 \times 10^{23}$ kW in all directions. The result is that the annual amount of energy the earth receives is (on average) 342 W/m² (Boeker & van Grondelle, 1995). About 31% of this incoming radiation is reflected back into space by the earth’s albedo. A small part of the remaining radiation is absorbed by the atmosphere and most of it (168 W/m²) warms the earth’s surface. The atmosphere of the earth contains powerful, and natural, greenhouse gases that absorb radiation.

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9 For this chapter excerpts were used from (Laan van der, 2005).
10 A more detailed explanation can be found in Environmental Physics (Boeker & Grondelle van, 1995).
11 The average of near surface air temperature over land and sea surface temperature.
12 Reflectiveness of the earth (as seen from space) caused by mostly clouds and the surface of the earth.
In general, greenhouse gases absorb the earth’s emitted infrared radiation determined by the quantum mechanical properties of the specific molecule. The incoming radiation is emitted mostly at wavelengths between 0.2 and 4.0 µm, primarily in the ultraviolet (UV), visible and near-infrared wavelength regions, (fig. 2.2). To maintain the energy balance, the earth re-emits the energy it absorbs, back into space. Because the earth is much colder than the sun, this energy is emitted at longer wavelengths. Most of this radiation is emitted in the wavelength range from 4 to 100 µm, which is the region generally referred to as longwave or infrared (IR) radiation. Gases like H₂O and CO₂ are relatively inefficient absorbers of solar radiation (left) but they are strong absorbers of outgoing (right) IR radiation, hence the name greenhouse gases.

![Figure 2.2](image)

**Figure 2.2:** The sun emits most of its energy at wavelengths between 0.2 and 4.0 µm. The earth re-emits the absorbed energy back into space to maintain an energy balance, mostly in the wavelength range from 4 to 100 µm. Although water vapour, carbon dioxide, and other greenhouse gases are relatively inefficient absorbers of solar radiation, they are strong absorbers of IR radiation. Note the comparatively weak absorption of much of the solar spectrum and the region of weak absorption from 8 to 12 µm, an important section of the earth’s longwave spectrum, referred to as the atmospheric window. Based on (MacCracken & Luther, 1985).

The natural conditions are so that the absorption of (natural) greenhouse gases result in a global average temperature of approximately 15°C. Without these greenhouse gases the average temperature on earth would only be about -18°C. This system of incoming and outgoing radiation has been in balance for thousands of years, altered only by natural phenomena as variation in solar flux and events as for example volcano dust or meteoric impacts. The balance of the climate system started to get significantly disturbed since the start of the industrial revolution of the 18th century. Since then, the concentration of emitted anthropogenic greenhouse gases has increased the amount of solar energy absorbed in the atmosphere thereby altering the energy budget of the earth. Besides an increase in greenhouse gases, another cause is a change in albedo as a result from land use changes, attributed to mostly increase in agriculture.
An externally imposed perturbation in the energy budget of the earth’s climate system is usually given in terms of the radiative forcing, expressed in W/m² (IPCC, 2001). A schematic description of this is shown in figure 2.3. To be more specific, radiative forcing is the change in the net vertical irradiance at the tropopause due to an internal change or a change in the external forcing of the climate system, such as, for example, a change in the concentration of carbon dioxide (CO₂) or the output of the sun. An increase in atmospheric CO₂ for example, leads to a reduction of the earth’s long wavelength emission at the top of the atmosphere by absorbing energy. The absorbed energy is re-radiated in all directions so that some of the radiation is lost in space and some of it is emitted downwards. The latter effect will lead to an entrapment of longwave radiation. Consequently, the flux at the top of the atmosphere will decrease. For the system to be stable, the energy balance at the top of the atmosphere requires a constant flux. To compensate for the decrease, the earth’s surface temperature should rise. A positive radiative forcing induces global warming, a negative value results in global cooling. At the moment, CO₂ is the most effective anthropogenic greenhouse gas contributing to global warming, whereas sulphur aerosols are an example for global cooling by reflecting solar shortwave radiation.

Table 2.1 shows the radiative forcing values for the most important anthropogenic well-mixed greenhouse gases and their abundances.

<table>
<thead>
<tr>
<th>Greenhouse gas</th>
<th>Abundance 1750</th>
<th>Abundance 1998</th>
<th>Radiative forcing (W/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>278</td>
<td>365</td>
<td>1.46</td>
</tr>
<tr>
<td>CH₄</td>
<td>700</td>
<td>1745</td>
<td>0.48</td>
</tr>
<tr>
<td>N₂O</td>
<td>270</td>
<td>314</td>
<td>0.15</td>
</tr>
<tr>
<td>SF₆</td>
<td>0</td>
<td>4.2</td>
<td>0.002</td>
</tr>
<tr>
<td>CO</td>
<td>50</td>
<td>160</td>
<td></td>
</tr>
</tbody>
</table>

The effect on global average surface temperature by changes in radiative forcing is still not completely understood. The relation between direct radiative forcing potential and global temperature is complicated by feedback systems as water vapour and albedo effects. It is clear, however, that an increase in greenhouse gases leads to an increase in radiative forcing, thereby warming the earth’s surface. This indicates also the need for more research on the topic to gain insight in the global abundance and regional distribution of greenhouse gases and their effect on the climate system.
2.1.1 Carbon Dioxide (CO$_2$)

Without any doubt, the most important anthropogenic greenhouse gas is Carbon dioxide (CO$_2$). The average global atmospheric CO$_2$ concentration has increased from 280 ± 10 ppm in 1800, to about 370 ppm in 1999. The first part of the increase was slowly but it has risen progressively faster, echoing the increasing pace of global agricultural and industrial development. Its present concentration has not been exceeded during the last 420,000 years. This recent and continuing increase of atmospheric CO$_2$ is attributed to anthropogenic emissions, mostly fossil fuel burning. Atmospheric O$_2$ is declining at a rate comparable with fossil fuel emissions of CO$_2$. Also, the characteristic isotope signatures of fossil fuel (which contains no $^{14}$C and is depleted of $^{13}$C) leave their mark in the atmosphere. And third, the observed increase in CO$_2$ concentration has been higher in the northern latitudes, where most of the fossil fuel burning takes place (IPCC, 2001).

Fossil fuel burning and land use changes are mainly responsible for altering the natural atmospheric CO$_2$ concentration. The atmospheric concentration from 1958 to 1994 is shown in figure 2.4. It indicates the high rate of increase of atmospheric CO$_2$. Since 1959, atmospheric CO$_2$ has increased by more than 40 ppm. About 75% of the anthropogenic emissions are attributed to fossil fuel burning, land use changes are responsible for the rest. These components represent imbalances in the large natural two-way fluxes between the atmosphere and ocean, and also between the atmosphere and land biota and south Pole. Globally, the atmosphere accumulates about 40% of CO$_2$ emitted by human activities; the rest is absorbed by oceans and the biosphere.

**Figure 2.4.** The average annual concentration of CO$_2$ in the atmosphere, from 316 ppm in 1959 to 358 ppm in 1994. Data from measurement stations Mauna Loa, Hawaii. Source (Wuebbles et al., 1997).

**Table 2.2:** Global CO$_2$ budgets (in PgC/yr) based on intra decadal trends in atmospheric CO$_2$ and O$_2$ concentrations. Positive values are fluxes to the atmosphere; negative values represent uptake from the atmosphere Source: (IPCC, 2001).

<table>
<thead>
<tr>
<th></th>
<th>1980s</th>
<th>1990s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atmosphere increase</td>
<td>3.3 ± 0.1</td>
<td>3.2 ± 0.1</td>
</tr>
<tr>
<td>Emissions (fossil fuel, cement)</td>
<td>5.4 ± 0.3</td>
<td>6.3 ± 0.4</td>
</tr>
<tr>
<td>Ocean-atmosphere flux</td>
<td>-1.9 ± 0.6</td>
<td>-1.7 ± 0.5</td>
</tr>
<tr>
<td>Land atmosphere flux total</td>
<td>-0.2±0.7</td>
<td>-.1.4±0.7</td>
</tr>
<tr>
<td>-Land use change</td>
<td>1.7 (0.6 to 2.5)</td>
<td>NA</td>
</tr>
<tr>
<td>-Residual terrestrial sink</td>
<td>-1.9 (-3.8 to 0.3)</td>
<td>NA</td>
</tr>
</tbody>
</table>
However, atmospheric CO$_2$ is only increasing by about half of the rate of fossil fuel emissions. It is partly taken up by the terrestrial ecosystems and dissolved in the oceans top layer and then mixed into the deep ocean, see table 2.2 and figure 2.5. More research is however needed (especially regionally) to determine the natural sinks absorptive capacity and how they will evolve over time (CarboEurope, 2004). Also, measurements of atmospheric CO$_2$ are needed to determine if the European efforts to reduce CO$_2$ emissions (Kyoto protocol) are detectable in the atmosphere. It has been proposed that Europe’s terrestrial biosphere absorbs 7 to 12% of Europe’s anthropogenic carbon emissions (Janssens et al., 2003).

Figure 2.5. The human perturbation of the global carbon cycle in PgC/Yr (data from Table 2.2). Fossil fuel burning and land-use change are the main anthropogenic processes that release CO$_2$ to the atmosphere. Only a part of this CO$_2$ stays in the atmosphere; the rest is taken up by the land (plants and soil) or by the ocean.
2.1.2 Carbon Monoxide (CO)

Carbon monoxide has an important role in the oxidizing capacity of the earth’s atmosphere, it may therefore indirectly affect the concentrations of many anthropogenic and natural trace gases, affecting climate, atmospheric chemistry and the ozone layer (Khall & Rasmussen, 1994). It affects atmospheric chemistry, primarily because of its chemical coupling with methane and the oxidants OH, \( \text{OH}_2 \), and \( \text{O}_3 \). Hydroxyl (OH) is formed from the photodissociation of tropospheric ozone and water vapour. OH radicals remove many man-made and natural trace gases from the atmosphere including halocarbons and hydrocarbons. OH radicals in the global atmosphere are removed primarily through reactions with CO. Thus, increases in CO may lead to decreases in OH and thereby indirectly resulting in an increase in concentration of anthropogenic and natural trace gases in the atmosphere (Khalil, 2004). As it is able to modulate the production of methane and tropospheric ozone, carbon monoxide itself is considered an indirect greenhouse gas, mostly because it does not absorb terrestrial thermal IR energy strongly enough. CO is produced by the oxidation of methane and other hydrocarbons and released into the atmosphere from automobiles, agricultural waste and burning of savannas. A recent study (Khalil, 2004) shows that human activities are responsible for over half of the annual emissions of CO. The atmospheric CO concentration in the 1980s was increasing at approximately \( 1.2 \pm 0.6\% \) per year. Since 1988, atmospheric CO concentration has been declining again at a rate of about \( 2.6 \pm 0.8\% \) per year (Khall & Rasmussen, 1994). One possible explanation is the reduction in vehicle emissions of CO due to more use of catalytic converters.

The Northern Hemisphere contains about twice as much CO as the Southern Hemisphere because as much as half of the global burden of CO is derived from human activity, which is predominantly located in the Northern Hemisphere. Due to the spatial variability of CO, it is difficult to ascertain global concentrations.

Figure 2.6 shows regional data measured in Scotland (Steele et al., 2003), an annual pattern of CO is evident, largely due to an increase in its destruction by the OH radical during the summer months. Additional influences include spatial and seasonal differences in source strength associated with varying trajectories of arriving air at different times of the year. Annual average mixing ratio at the Shetland Islands for 2001 had decreased by about 7 percent of the 1993 value; however, no long-term trend is clearly evident.
2.1.3 Methane (CH$_4$)

The second-most important greenhouse gas is methane (CH$_4$), see table 2.1. The average global atmospheric concentration is currently about 1750 ppb (fig 2.7). The current level of atmospheric concentration indicates a more than doubling of the pre-industrial value of 700 ppb (IPCC, 2001). The atmospheric concentration of CH$_4$ in the Northern Hemisphere is approximately 100 ppb higher than in the southern Hemisphere. This suggests that there are greater sources or/and smaller sinks in the northern part of the earth (Houghton et al., 1992). Approximately 70% of the total CH$_4$ production is attributed to purely anthropogenic sources and 30% is believed to be from natural sources. The major source of CH$_4$ is biological generation in anaerobic environments. This includes natural and man made wetlands, enteric fermentation and anaerobic waste processing (Mosier et al., 2004). Other sources of CH$_4$ emissions are: rice paddies, termites, gas plants, transport, mining, gas usage and biomass burning.

![Figure 2.7: Change in CH$_4$ abundance (mole fraction, in ppb = 10$^{-9}$) determined from ice cores, firn, and whole air samples plotted for the last 1,000 years. Radiative forcing, approximated by a linear scale since the pre-industrial era, is plotted on the right axis. Source: (IPCC, 2001).](image)

The primary sink for CH$_4$ is reaction with the OH radicals in the troposphere:

$$\text{OH} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{H}_2\text{O}$$  \hspace{1cm} (2.1)

Aerobic soils oxidize 10-20% of the total CH$_4$ production. Further, a stratospheric sink of about 10% of production is suggested (Mosier et al., 2004). The atmospheric residence time of CH$_4$ is derived to be about approximately 8.4 years. Since 1990, the annual rate of CH$_4$ increase in the atmosphere has varied between less than zero and 15 ppb. The reason or reasons for this variation are still not exactly known (Rudolph, 1994).
2.1.4 Nitrous Oxide (N\textsubscript{2}O)

Nitrous oxide (N\textsubscript{2}O) is the third most important anthropogenic greenhouse gas. Furthermore, N\textsubscript{2}O is also involved in the depletion of the O\textsubscript{3} (ozone) layer in the stratosphere, which protects the biosphere (including humans) from the harmful effects of solar ultraviolet radiation. It has been suggested that a doubling in N\textsubscript{2}O concentration would lead to a 10% decrease in the ozone layer. This would increase the amount of ultraviolet radiation reaching the earth by about 20% (Crutzen & Ehhalt, 1977). The pre-industrial atmospheric concentration was about 275 ppb but has increased to approximately 317 ppb, see figure 2.8. Most of this increase occurred during the past 50 years with an almost linear increase of 0.7 ppb/year (Mosier et al., 2004). N\textsubscript{2}O abundances tend to be about 0.8 ppb higher in the Northern Hemisphere than in the Southern Hemisphere, consistent with about 60% of emissions occurring in the Northern Hemisphere (IPCC, 2001).

![Figure 2.8](image)

Figure 2.8: Change in N\textsubscript{2}O abundance for the last 1,000 years as determined from ice cores, firm, and whole air samples. Radiative forcing, approximated by a linear scale, is plotted on the right axis. De-seasonalised global averages are plotted in the inset. Source: (IPCC, 2001).

It has been estimated (Kroeze et al., 1999) that the global N\textsubscript{2}O emissions in 1994 were approximately 17.6 Tg, with 9.6 Tg (55%) of the total arising from relative natural terrestrial and aquatic systems and about 8 Tg derived from anthropogenic sources. Approximately 70% of the latter is attributed to agriculture, both crop and livestock production. N\textsubscript{2}O is for example emitted in response to Nitrogen fertilisation. The rest can be attributed to nylon production, nitric acid production, power plants and vehicular emissions. The expected atmospheric residence time of N\textsubscript{2}O is believed to be approximately 114-120 years. As with methane, it remains difficult to access global emission rates from individual source that vary greatly over small spatial and temporal scales (IPCC, 2001).
2.1.1 Sulphur Hexafluoride (SF$_6$)

Sulphur Hexafluoride (SF$_6$) is a very stable, almost entirely anthropogenic (some traces originate from fluorite rocks) trace gas (Burgess et al., 2004). Its unique physical and chemical properties make it an ideal gas for many applications, predominantly in electrical insulation (Maiss & Levin, 1994). SF$_6$ is an extremely powerful, on a per molecule basis, greenhouse gas. It is a thousand times as effective as CO$_2$. The contribution of SF$_6$ to radiative forcing is still very small because its atmospheric concentration is currently less then 5 ppt. Even so, it has an high effectiveness as a greenhouse gas, together with its atmospheric lifetime of approximately 3200 years (Ravishankara et al., 1993) give it the potential to become a significant contributor to radiative forcing in the (near) future. The only known important sink for SF$_6$ is photolysis or ion reactions in the mesosphere (IPCC, 2001).

![Figure 2.9: Abundance of SF$_6$ (ppt) measured at Cape Grim, Tasmania since 1978 (Maiss et al., 1996; Maiss and Brenninkmeijer, 1998). Cape Grim values are about 3% lower than global averages. Source: (IPCC, 2001).](image)

Until approximately 1990, the atmospheric concentration of SF$_6$ has been increasing by about 7-8% per year (Maiss et al., 1996), see figure 2.9. Recent studies however, indicate that the increase in emission, if not production, has slowed down the past few years (Connell et al., 2000; Maiss & Brenninkmijer, 1998). SF$_6$ has been shown to be an ideal tracer for the validation of the long-range transport properties of atmospheric models (Levin & Hesshaimer, 1996), making it an ideal candidate for in-situ measurements at Lutjewad.

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13 Chemical process by which molecules are broken down into smaller units through the absorption of light.
CHAPTER 3: GAS CHROMATOGRAPHY

To be able to distinguish between the different trace gases in both a quantitative and qualitative way, a HP Agilent 6890 gas chromatograph was used. In this chapter the basics of (gas) chromatography are briefly explained. Since this device is being used at the limits of its capabilities, a major part of the research time was used in order to make it work properly. The complications that were to be resolved are also discussed in this chapter.

3.1 Theoretical introduction

Gas chromatography (GC) is a method used for separating a mixture of compounds (solutes) into separate compounds, and measuring the relative quantities of these substances. When separated, the individual substances can be identified (qualitative) and their amount (quantitative) can be determined. It is a highly accurate technique and can be used even when only a very small quantity of sample is available. The basic components of a GC system are an oven, a column and a detector, see figure 3.1. In the case of gas chromatography, the gas sample consisting of for example, outside-air, is flushed through a sample loop and then transported by a carrier gas through a (packed) column. The column is basically a stainless steel tube that is packed with a material that has a different adsorption strength towards the different gases in the sample. The fastest moving solute exits (elutes) the column first, then followed by the remaining solutes in corresponding order. After each solute is eluted from the column, it enters a (heated) detector that analyses the different substances. For example: consider a sample of air containing 78% N\textsubscript{2}, 20.95% O\textsubscript{2}, 0.95% Ar, 0.035% CO\textsubscript{2}, and 1.8ppm CH\textsubscript{4}. If injected into a carrier gas and transported through a column of Haysep N\textsuperscript{14}, then the N\textsubscript{2}/O\textsubscript{2}/Ar goes through the column first, closely followed by CH\textsubscript{4} and then CO\textsubscript{2} because Haysep N has very little affinity for N\textsubscript{2}/O\textsubscript{2}/Ar, some affinity for CH\textsubscript{4} and a great affinity for CO\textsubscript{2}. By varying column packing it is possible to separate different mixtures of gases.

![Figure 3.1 a: Basic description of a chromatograph. It basically consists of a column, an oven and a collector. In the case of a gas chromatograph, the sample gas is pumped in a sample loop (injector part) and then flushed on the column by a carrier gas.](image)

![Figure 3.1 b: Snapshot of the Agilent HP6890N gas chromatograph. Shown in this picture are the columns in the oven part of the GC, the manual control panel and on top of the GC the pneumatically driven actuators for controlling the valves.](image)

The time needed for each substance to leave the column is called ‘retention time’ and under the same circumstances (carrier pressure, temperature etc.) the retention time remains the same for each measurement. If the amount of the substance varies, only the height of the signal and its surface will change, which makes identification and measuring its amount possible for different substances. The gas chromatograph used in this research is the HP Agilent 6890N, initially equipped with two 10 ml sample loops, one 12’ Haysep Q column for CO\textsubscript{2}/CH\textsubscript{4} detection and two Haysep Q (4’ and 6’) columns for N\textsubscript{2}O/SF\textsubscript{6} detection. The first substances are measured with a FID detector, the latter with an ECD. The signal is then plotted and recorded on a computer. A detailed explanation of the different parts will follow in the next chapters.

\textsuperscript{14} Packing material of column
3.2 The Flame Ionisation Detector (FID) and Nickel Catalyst Methanizer

For detection of CO\(_2\) and CH\(_4\), the sample is, together with the carrier gas (N\(_2\)), led through a hydrogen (H\(_2\)) flame after it has left the column, see figure 3.2. The flame produces a few ions, but when it burns an organic compound, an increase in ions is produced. A polarized voltage is used to lead the ions to a collector near the flame. This produces a current between the electrode on which the voltage is applied and the electrode of the collector which is proportional to the amount of ions, and thus of sample that is burned. An electrometer measures this current. The measured current is digitalised and displayed on a computer.

In order to achieve combustion, the sample has to be of organic material like for example CH\(_4\). In order to detect CO\(_2\), the sample has to be converted to CH\(_4\). This is done by leading the sample through a tube packed with nickel catalyst powder: a catalyst. In the catalyst, CO\(_2\) is mixed with H\(_2\) to form CH\(_4\) at a temperature of 375 °C. This is an organic compound, capable of being combusted to CO\(_2\) and H\(_2\)O in the FID.

\[
\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \quad (3.1)
\]

Since the conversion of CO\(_2\) to CH\(_4\), see equation (3.1), occurs after the sample compounds has passed through the column, its retention time remains unchanged.
3.3 The Electron Capture Detector (ECD)

An Electron Capture Detector (ECD) (fig. 3.4) was used for measuring N$_2$O and SF$_6$. The ECD contains a radioactive source. It consists of a cell plated with $^{63}$Ni, a radioactive isotope with a half-life time of 100 years, that produces high energy electrons ($\beta^-$ particles). The beta particles collide and interact with the carrier gas molecules producing low energy electrons. Each beta particle produces approximately 100 free electrons. The free electrons produce a small current $^{15}$, which is then collected and measured in a pulsed circuit. When a molecule from a sample comes into contact with these free electrons, the sample molecules may capture some of them to create negatively charged ions. A voltage is pulsed across the cell electrodes to collect the remaining free electrons. The heavier ions are relatively unaffected and swept out with the carrier flow. The cell current that is measured is compared to a reference current. The difference between the two is used to adjust the pulse rate to keep both current equal. When there are more free electrons, there is lower pulse frequency required to match the reference current. A component that captures electrons passes through the cell, causing a decrease in the electron concentration and hence, an increase in the pulse rate. This pulse rate is then converted to a voltage and recorded or displayed on the computer screen. Thus, the amount of free electrons left is a measure for the amount of sample molecules (Agilent, 2004).

$^{15}$ Reference-, or standing current

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Figure 3.4. The Electron Capture Detector (ECD). Sample molecules are transported with the carrier gas along a radioactive source. The sample molecules capture some of the electrons that are produced by the $^{63}$Ni source.
CHAPTER 4: INITIAL CONFIGURATION AND OPTIMISATION

Before the start of this research, the gas chromatograph was installed by a technician from Agilent. It was tested by injecting large quantities of test samples of CO$_2$, CH$_4$, N$_2$O and SF$_6$. Since the CIO was going to use the device for in-situ measurements of extremely small amounts of trace gases, additionally adjustments were to be made. The GC however, proved to have several significant ‘bugs’, making it impossible to work properly. In this chapter, it is discussed how these problems were solved and which further adjustments were made. First, we will start by discussing the initial configuration of the GC.

4.1 INITIAL CONFIGURATION

The gas chromatograph actually consists of two separate systems: one system using the ECD and another system using the FID. Both systems have their own sample loop, sample injection valve, column(s), and their own carrier gas. They share one oven for heating the columns and one sample inlet flow controller. The initial configuration of the system can be seen in figure 4.1. It shows the four 6-port/2-state valves (4/701, 1/705, 3/701 and 2/700), the two detectors (ECD and FID), the methanizer (CAT), two sample loops, three columns and three gas inlets$^{16}$ aux 3 to 5 and the (PCM) front inlet controller. The sample air enters the system through aux 5, and flushes first the FID sample loop and then the ECD sample loop. In the mean time, the carrier gases flush the columns producing a steady baseline for the ECD and FID detectors. This mode is called the ‘load phase’ since the sample loops are loaded with sample air.

![Figure 4.1: Schematic representation of the Gas Chromatograph. Nitrogen (N$_2$) is used as a carrier gas for the FID detector (aux 4) and as a backflush gas for the ECD analytical column (aux 3). A mixture of Argon/Methane is used as a carrier gas for the ECD (front inlet/PCM). The sample air enters the system through aux 5.](image)

The ECD system is switched to the ‘inject phase’ by switching valve 4 (4/701). In this case, the carrier gas (front inlet/PCM) is lead through the sample loop, injecting the sample into the columns. The carrier gas (N$_2$) has to be as clean as possible$^{17}$ to avoid contamination of the columns.

---

$^{16}$ Consisting of flow- or pressure controllers.

$^{17}$ At least 5.0.
This system consists of two columns: a 4 feet pre-column and a 6 feet analytical column of 3/16 inch, both Haysep Q packed, and mesh size 80/100. After elution of N\textsubscript{2}O and SF\textsubscript{6} from the pre-column, valve 1 is switched and the pre-column is backflushed (aux 3), removing any unwanted slowly moving substances left. The remaining sample passes through the analytical column and enters the ECD, N\textsubscript{2}O first, and then closely followed by SF\textsubscript{6}.

The FID system is similar to the ECD system. After flushing the sample loop, valve 3 is switched, putting the system in the inject mode. The carrier gas (aux 4) is a mixture of pure argon (95%) and methane (5%). The carrier gas leads the sample air through a 10 feet Haysep Q column (also 3/16 inch and mesh size 80/100) separating the different compounds in the air. To be able to detect CO\textsubscript{2}, the sample is lead through the catalyst after elution of CH\textsubscript{4} from the column by switching valve 2.

4.2 REPAIRS AND OPTIMISATION

After a few weeks, it became clear that the GC was not able to work properly, indicating improper construction and installation by the factory. One of the main problems we had was that the baseline of the ECD was highly unstable and was increasing daily. As a result, the software was not able to integrate the N\textsubscript{2}O and SF\textsubscript{6} peaks in the chromatogram. From our colleges from ECN\textsuperscript{19}, who have a somewhat similar GC setup at their atmospheric measurement tower in Cabauw, we learned that the most plausible cause for this instability would most probably be an impure (4.5\textsuperscript{20}), although installed by Agilent, ECD carrier gas. This was later confirmed by Agilent. The problem was fixed by installing an Argon/methane carrier gas with a purity of 6.0. Also, the ECD inlet was cleaned and reinstalled. The FID system was also very unstable. The CO\textsubscript{2} peak was tailing, and the total measurement time was about 12 minutes. It became clear that the columns had never been conditioned properly by Agilent and that some filling from the columns was blocking the FID inlet Jet. We therefore ‘baked’\textsuperscript{21} the columns and cleaned the FID inlet. Doing so, we noticed that the 1/16” tube between the 3-way splitter and the FID inlet had an extremely small internal diameter. We replaced this tube with ‘normal’ tube.

These repairs resulted in a complete, and reproducible measurement of both CH\textsubscript{4} and CO\textsubscript{2} within 3 minutes. During these repairs, we noticed that most of the Swagelok\textsuperscript{22} connections (fig. 4.2) were incorrectly assembled. Once loosened, they could not be reassembled again without leaking. All of the connectors had to be reassembled with new Swagelok connectors. After these repairs, the GC responded properly and it was able to measure the desired trace gases within 4.5 minutes. However, we estimate a delay of approximately 7 weeks which we attribute to improper assembly and/or installation by Agilent.

\textsuperscript{18} See appendix VI for a detailed description.
\textsuperscript{19} Energy research Centre of the Netherlands, Petten.
\textsuperscript{20} A purity of 4.5 means that the gas is 99.995% pure, 5.0 means 99.999%.
\textsuperscript{21} Heating the columns at a temperature of about 200°C to de-contaminate the packing.
\textsuperscript{22} Brand name of the connectors for tubing and columns, typical for GCs.
As shown in figure 4.1, the sample air enters the system through aux 5 which is an internal pressure controller. Its function is to make sure that the sample loops are always flushed with the same flow rate, independent from the source, which can be either the atmospheric measurement tower or a reference gas from a cylinder. Also, after the sample loops are flushed with slight overpressure, the sample air needs some time to equilibrate with the atmospheric pressure before it is lead to the columns to assure that the amount of molecules is the same between two successive measurements. Thus, the sample air must be able to be stopped. The maximum flow rate possible with the aux 5 pressure controller however was only about 15 ml/min at a pressure of about 30 psi (about 2 bar). Considering the sample loops and tubing, the time to completely flush the system would be more than 2 minutes. This same setup was also used for atmospheric measurements in the region of Saclay, France (Pepin et al., 2000), where a flow rate of 125 ml/min was obtained with only 2.5 psi (about 0.18 bar). Since Agilent was not able to explain this difference, or provide a useful solution, we decided to use an external mass flow controller (100 ml/min) for the sample air. This mass flow controller can be controlled by the GC software. By switching ‘valve 8’, a (normally open) relay contact is closed, bypassing the resistor of the mass flow controller (see appendix III), reducing the flow rate of the sample air to zero.

The chromatograms of both the ECD and FID system are shown in figures 4.3 and 4.4. They represent atmospheric measurements taken at Zernike, Groningen, early June 2005. The gas chromatograph is able to measure CH$_4$, CO$_2$, N$_2$O and SF$_6$ within 4.5 minutes, including flushing the sample loops.

![Chromatogram of the ECD system. The y-axis is presented in Hz (detector output), the x-axis is in minutes. The first peak indicates O$_2$ followed by N$_2$O and SF$_6$. A complete measurement including flushing of the sample loops was obtained within approximately 4.5 minutes.](image)

The first peak shown in the chromatogram of the ECD (fig. 4.3) represents oxygen (O$_2$). This peak is not reproducible enough to include O$_2$ in the measurements. It is even suggested (Jordan et al., 2004) that this large amount of O$_2$ can cause a drift in the sensitivity of the ECD or potentially even be harmful (Agilent, 2004). The second peak represents N$_2$O, and the third SF$_6$. The latter is a very small peak since its atmospheric concentration is in the order of parts per trillion (ppt).
In the chromatogram of the FID system (fig. 4.4) we also notice an O$_2$ peak (at t=0.8) however it is much smaller. It also does not seem to affect the sensitivity provided it does not come into contact with the Nickel Catalyst. The second peak represents CH$_4$. After this is eluted from the column and registered by the detector the sample is re-routed through the Catalyst by switching valve 2. The switching of this valve produces a spike in the chromatogram at 1.5 minutes. Because the switching induces a flow rate change, it leads to a higher baseline. The CO$_2$ is then methanized and detected by the FID.

### 4.3 Implementation of an Oxygen Bypass Switch for the ECD

In order to reduce any (potentially) harmful effects of O$_2$ on the ECD, an O$_2$ bypass valve was installed. Agilent offers a special bypass valve called the ‘Deans Switch’ that can be controlled by the Chemstation software. In the chromatogram, it is possible to choose an area or peak that needs to be removed, and the switch then pilots it through a ventilation tube. A much less expensive way is by replacing one of the two 6 port valves with a 10 port valve. The load, inject and backflush modes can then be controlled by only one 10 port/two position valve. The other 6 port/two position valve can then be used for bypassing the detector.
Figure 4.5: Reconfiguration of the ECD system. Loading, injecting and backflushing are controlled by only one 10 port valve. A second, 6 port, valve can then be used to bypass O$_2$ from the ECD.

In the load phase (fig. 4.5) the sample airflow is controlled by mass flow controller B and flushes the sample loops with approximately 100 ml/min. In the mean time, the pre-column is backflushed with the carrier gas which enters the system through the front inlet. The analytical column is simultaneously flushed with the carrier gas controlled by mass flow controller A. Dependent on the position of valve 1, either the pre-column, or the analytical column is connected to the ECD. By switching valve 4, first the carrier gas flows through the sampleloop, next through the pre-column and finally the analytical column and is then vented out. After O$_2$ has eluted from the analytical column, valve 1 is switched so that N$_2$O and SF$_6$ can be detected by the ECD. Since valve 4 also backflushes the pre-column when switched in the load position, it can only be switched after both N$_2$O and SF$_6$ have eluted both from the pre-column.

When replacing the 6 port valve with an 10 port valve, an adjustment to the switching angle of the actuator must be made. To switch a 6 port valve, the actuator has to switch an angle of 60$^\circ$, but the 10 port requires a maximum angle of 36$^\circ$. For this reason, a 36$^\circ$ actuator limiter (Agilent, order number 18900-21000) was installed on the actuator that controls valve 4. Figure 4.6 shows the internal valve box of the gas chromatograph. In it, there are the four valves (V1, V2, V3 and V4) that are described in this chapter. The valves are kept at a constant temperature of about 70$^\circ$ C in order to omit varieties in the measurements due to outside temperature changes.

Figure 4.6: The valve box of the GC containing the 4 valves.
Figure 4.7: The chromatogram of the ECD system when an O\textsubscript{2} bypass valve is installed only a small spike remains indicating the switching of the bypass valve to normal operation. The O\textsubscript{2} is vented out of the system. After O\textsubscript{2} has passed the bypass valve is switched back again in order to detect N\textsubscript{2}O and SF\textsubscript{6}. The change in baseline height is caused by pressure changes.

The end result is shown in figure 4.7. The oxygen peak is removed from the chromatogram and is no longer contaminating the ECD. The difference in baseline level can be attributed to the differences in resistance that the carrier gas experiences when valve 1 is switched. A small spike indicates the switching of the O\textsubscript{2}-bypass valve. After the oxygen has passed, the bypass switch is switched back in order to detect N\textsubscript{2}O and SF\textsubscript{6}. The baseline needs about half a minute to recover again from the pressure difference after switching the O\textsubscript{2}-bypass valve off. Nevertheless, stability is obtained again, in time, at about 3.2 minutes.
CHAPTER 5: IMPLEMENTATION OF CARBON MONOXIDE (CO)

Besides the continuous measurements of atmospheric CO₂, CH₄, N₂O and SF₆, the Centre for Isotope Research (CIO) also has a strong interest in measuring Carbon monoxide (CO) at Lutjewad. Therefore, in order to also measure CO, a second device would be needed capable of measuring CO. In principle the FID of this GC is also capable of measuring CO if the right columns are used. However, the GC is equipped with only one FID and one oven, and all of the pressure and flow controllers, sample loops and valves are already in use to detect CO₂, CH₄, N₂O and SF₆. This chapter describes how the GC was modified and improved so that besides CO₂, CH₄, N₂O and SF₆ also CO can be measured.

To be able to make relevant correlations, it is important that the CO measured by the GC is from the same sample air as CO₂, CH₄, N₂O and SF₆. One possibility is to install a second GC, perhaps with only one FID detector, and couple it to the first GC (Pepin et al., 2000). We decided to improve our GC and extend it with two additional columns, two external (heated) valves (fig. 5.2, fig. 5.3) and an extra sample loop. The new FID system is shown in figure 5.1.

Figure 5.1: Reconfiguration of the FID system. The part for the CO₂ and CH₄ is basically the same. Valve 5 switches the FID to either the CO₂ and CH₄ part, or the new part that separates CH₄ and CO with a Porapak Q pre-column, and a Molsieve 5A analytical column.

The carrier gas flows (both N₂) are controlled by the internal pressure controllers aux 5 and aux 3. An extra sample loop (5 ml) was installed on the sample loop heater. The 5 ml sample loop is used for the CO₂/CH₄-line, and the original 10 ml sample loop was used for the CH₄/CO-line. The largest sample loop (larger amount of sample) was used for the CO-line since CO has a much smaller atmospheric concentration CO₂ and CH₄. The CH₄/CO₂ part (lower part of the scheme) is still the same, the only difference is that the Haysep Q column is not directly connected to the FID (valve 2), but first goes through valve 5. The CH₄/CO-line (upper part) is almost identical to that of the ECD system. The load, inject and backflush-phases are all controlled by one 10 port/two position valve (V6).
The CH₄/CO-line consists of a 6 feet pre-column (Porapak Q, 1/8 inch, mesh size 80/100) and a 4 feet analytical column (Molsieve 5A, 1/8 inch, mesh size 60/80). The function of the Porapak Q column is to prevent CO₂ from entering the Molsieve 5A. CO₂ has the potential to inactivate the chemical compound of the Molsieve column. The Porapak Q column separates a mixture of CH₄ and CO from the sample air. After this mix has eluted the Porapak Q column, and enters the Molsieve column, valve 6 is switched to the ‘load’ position again; backflushing the Porapak Q column. CO₂ and other (unwanted or undesired) compounds are flushed out and further separation of the CH₄/CO mixture takes place in the Molsieve 5A column.

Figure 5.2: The external valves and actuators V5 and V6 are mounted on top of the GC. In the front, valves 1 to 4 are visible

Figure 5.3: Side view of the external valves. The valves are kept at a relative constant temperature by using the waste heat from the Catalyst.

In order to omit varieties in the measurements due to outside temperature changes, the external valves (v5 and v6) should be kept at a constant temperature. Therefore, the waste heat of the catalyst was used to warm the valves, by mounting the valves on top of the gas chromatograph. The top of the catalyst, which is kept at a constant temperature, is accessible from the top of the GC. This made it possible to use its waste heat by mounting a box around it, which included also the valves 5 and 6. The temperature inside the box is about 65°C, about the same as that of the internal valves.

Figure 5.4: Chromatogram of the FID after the improvements were made. First, O₂ elutes from the CO-line (see enlargement). Next, the Catalyst is switched on (spike) and CH₄ and CO are measured. At t=3 minutes valve 5 is switched on, in order to detect the gases in the CO₂ line, and the Catalyst is bypassed to prevent O₂ contamination. After the O₂ has eluted from the Haysep column, CH₄ is measured by the FID. Then the Catalyst is switched on again and finally CO₂ is measured. The long tailing of the CO₂ peak prevents a complete measurement in 5 minutes. Instead, a complete measurement, including the equilibrium time needed for the sample flush, is completed within 6 minutes.
By switching valve 5 (fig. 5.4), a choice is made between either detecting the sample that elutes from the Haysep Q column (CH\textsubscript{4}/CO\textsubscript{2}), or the Molsieve 5A column (CH\textsubscript{4}/CO). By altering the time of injection, it can be determined at what time the CH\textsubscript{4} and CO\textsubscript{2} peaks appear in the chromatogram. The time of injection is chosen such that the CO-line is measured first, and then the CH\textsubscript{4}/CO\textsubscript{2} line is measured. This order proved to be the most stable solution. After an equilibrium time of 0.5 minutes\textsuperscript{23}, valves 4 (ECD) and 6 (FID, CH\textsubscript{4}/CO-line) are switched, injecting the sample air in their sample loops. At t = 2.5 minutes, valve 3 is also switched, injecting the sample for the CH\textsubscript{4}/CO\textsubscript{2}-line. After CO is measured, valve 5 is switched at t = 3 minutes in order to detect the CH\textsubscript{4}/CO\textsubscript{2}-line. To maintain a stable baseline, the catalyst is switched on already before CH\textsubscript{4} elutes from the columns. Switching valve 5 after the O\textsubscript{2} peak has eluted appeared to initiate instability of the baseline for about 1 minute. Table 5.1 shows the time table for the method that was used to obtain the measurement of CO, CH\textsubscript{4}, CO\textsubscript{2}, N\textsubscript{2}O and SF\textsubscript{6}.

Table 5.1: Time table of the GC method that was used for measuring CO, CH\textsubscript{4}, CO\textsubscript{2}, N\textsubscript{2}O and SF\textsubscript{6}.

<table>
<thead>
<tr>
<th>Time</th>
<th>Specifier</th>
<th>Parameter</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>Valve 8</td>
<td>On</td>
<td>Sample flush stop</td>
</tr>
<tr>
<td></td>
<td>Valve 1</td>
<td>On</td>
<td>ECD bypass on</td>
</tr>
<tr>
<td></td>
<td>Valve 5</td>
<td>Off</td>
<td>FID switch to CO-line</td>
</tr>
<tr>
<td>0.50</td>
<td>Valve 4</td>
<td>On</td>
<td>Inject (ECD)</td>
</tr>
<tr>
<td></td>
<td>Valve 6</td>
<td>On</td>
<td>Inject (CO-line FID)</td>
</tr>
<tr>
<td>1.50</td>
<td>Valve 6</td>
<td>Off</td>
<td>Load/backflush (CO-line FID)</td>
</tr>
<tr>
<td>2.00</td>
<td>Valve 2</td>
<td>On</td>
<td>Catalyst on</td>
</tr>
<tr>
<td>2.35</td>
<td>Valve 1</td>
<td>Off</td>
<td>ECD bypass off</td>
</tr>
<tr>
<td>2.50</td>
<td>Valve 3</td>
<td>On</td>
<td>Inject (CO\textsubscript{2}-line FID)</td>
</tr>
<tr>
<td>2.98</td>
<td>Valve 2</td>
<td>Off</td>
<td>Catalyst off</td>
</tr>
<tr>
<td>3.00</td>
<td>Valve 5</td>
<td>On</td>
<td>FID switch to CO\textsubscript{2}-line</td>
</tr>
<tr>
<td>3.65</td>
<td>Valve 3</td>
<td>Off</td>
<td>Load (CO\textsubscript{2}-line FID)</td>
</tr>
<tr>
<td>3.80</td>
<td>Valve 2</td>
<td>On</td>
<td>Catalyst on</td>
</tr>
<tr>
<td>5.00</td>
<td>Valve 4</td>
<td>Off</td>
<td>Load/backflush ECD</td>
</tr>
<tr>
<td>5.45</td>
<td>Valve 8</td>
<td>Off</td>
<td>Start sample flush loops</td>
</tr>
<tr>
<td>5.95</td>
<td>Valve 2</td>
<td>Off</td>
<td>Catalyst off</td>
</tr>
<tr>
<td>5.98</td>
<td>Valve 5</td>
<td>Off</td>
<td>FID switch to CO-line</td>
</tr>
<tr>
<td></td>
<td>Valve 8</td>
<td>On</td>
<td>Sample flush stop</td>
</tr>
</tbody>
</table>

\textsuperscript{23} This requires valve 8 to be labelled as the ‘injection valve’ since the GC software demands an injection at t=0.
In order for this system to work properly, a purifier (fig. 5.5) should be installed between the carrier gas supply (N$_2$) and the GC. Even though the carrier gas has a high purity of itself (5.0), an additional purifier proved to be indispensable when measuring CO. Not installing a purifier did not seem to have any notable effect on CH$_4$ or CO$_2$, however the CO peak was only visible after installation of a gas-purifier. When no purifier was installed, a ‘dip’ in the baseline occurred at almost exact the same retention time as CO, and was large enough to suppress the CO peak. The purifier used for purifying the carrier gas was the Aeronex 500K. It removes several gaseous condiments to sub-ppb levels and has a filter capable of removing 99.9999999% of particles 0.003 micron or larger.

The effect of the purifier is indicated by figure 5.6. It represents a combined chromatogram of four different measurements of the same sample air (flask) on the Agilent HP 6890N GC that is used in the CIOL lab to measure flasks from measurements stations. Line ‘a’ represents a measurement when no purifier was installed between the carrier gas cylinder and the GC. It shows a normal CH$_4$ peak, followed by a negative peak at about the same location where the CO is expected.

The line ‘b’ represents a measurement also without purifier, but the sample is now replaced with the carrier gas. In this case, also a disturbance in the baseline is seen, indicating that the source of this ‘dip’ has to be the carrier gas itself. When using a purifier for the carrier gas, the ‘dip’ is not present, and when measuring normal air (line ‘c’, the CO peak is clearly present. When using the carrier gas as sample air and a purifier for the carrier gas, the baseline is completely stable. Notice that the CO peak, and the opposite peak or ‘dip’, both have practically the same size and retention time.

Finally, the measurement from ‘a’ was repeated, also with the purifier installed. This is illustrated with line ‘c’. After the CH$_4$ peak, a normal CO peak is now also visible. Notice that both the CO peak, and the negative peak, or ‘dip’, both have practically the same size and retention time.
Chapter 6: Test results

After the gas chromatograph was equipped with an Oxygen bypass valve, and modified to include carbon monoxide in the measurements, it was tested by measuring a cylinder with known concentrations of CO, CO$_2$, and CH$_4$\textsuperscript{24}. Also, measurements were done to determine the stability of the GC.

6.1 Determination of calibration intervals

In order to acquire insight in the stability of the GC, several measurements were done. First, the GC measured one cylinder (7888) containing atmospheric air from the measurement site at Lutjewad. This cylinder was continuously measured for one day. The results are shown in figures 6.1 to 6.6. The results are uncalibrated, therefore, the x-axis represents the time of the day and the y-axis is presented in either pA (FID system) or Hz (ECD).

\textsuperscript{24} At the time of writing, no references were available for N$_2$O and SF$_6$. 
Measuring only one cylinder is used to gain insight in the drift of the system, and to determine how often a standard reference cylinder has to be measured to cancel out the fluctuation in the mean trend of the results. The fluctuation can originate from a drift in the GC, but also from an external source. This could be related to, for example, temperature or pressure differences in the laboratory (the sample is equilibrated to ambient air pressure in the sample loops before measuring) or contaminated fittings. However, we attribute the bulk part of the errors to the integration software. Parameters settings were not fully optimised, resulting sometimes in incorrectly integrated peaks in the chromatograms. An example of this is shown in figure 6.7. In this example, a too large area is integrated, giving too high concentration values. This error is fine-tuning problem, and can easily be adjusted. A combination of errors can occur when for some reason the software completely misses a peak. In this case, the whole sequence of integration is disturbed, causing, the software to confuse the different compounds with each other. The software designed at the CIO that reads the data from the files that are created by the GC and converts it into one excel file, is at this stage, not yet capable of taking this into account.

![Figure 6.7: Screenshot of the CH₄ peak (CO₂ line) indicating an error in the integration of the peak, see zoomed-in area. The surface area of the peak is registered higher than it actually is giving too high concentration data.](image)

Figures 6.1 to 6.6 give already some insights in the stability of the GC. The drift seems to be different for each trace gas. This suggests that the drift is not solely caused by the GC, but perhaps also has an external cause. There is also a lot of noise in the data, especially in the substances with the smallest concentration. The SF₆ peak for example suffers from the noise in the carrier gas, even though this has an extreme high purity (6.0). SF₆ is measured in parts per trillion and even a very small disturbance will be immediately visible. In some of the results, a periodical trend is visible. This trend can be cancelled out by measuring a reference cylinder with well-known concentrations. The periodicity of the measurement with this reference cylinder depends on the trend in the measurements. To determine how often a calibration cylinder has to be measured, we calculated the change in standard uncertainty for several calibration intervals. At normal operation, we determine the concentration of the sample using two calibration points from cylinders with well-known concentrations. For example, first we measure a cylinder with a higher than average concentration (7888), then 4 times the sample (outside air), and finally a reference with a lower than average concentration (9946). Assuming the difference between the two calibration gases (delta) remains the same, we can determine the concentration of the samples. However, figures 6.1 to 6.6 indicate a significant drift of the system and the two calibration...
gases have to be measured periodically to cancel out this fluctuation. When more samples are measured between the calibration gases, the drift between these two calibration points will increase, resulting in a higher uncertainty in the determined concentration of these samples. In other words: measuring only one sample between the two calibration gases (Reference, sample, Reference) decreases the time between calibration and reduces the drift between the two calibration points. The sample can be determined with a higher accuracy than with for example two (RssR) or three (RssssR) samples between calibrations but it dramatically reduces the number of measurement points.

To determine the decrease in accuracy as a function of calibration intervals, we simulated several measurement sequences (eg. RsR, RssR etc.) while measuring one calibration cylinder continuously. The change in standard deviation in the calibrated sample is then a measure for the maximum amount of samples that can be measured between two calibration points.

Using two calibration points\(^25\) and one sample (RsR) the concentration of the sample is given by:

\[
\text{concentration ref.} \cdot \frac{\text{area sample}}{\left(\frac{1}{2} \cdot \text{area ref. 1} + \frac{1}{2} \cdot \text{area ref. 2}\right)}
\]  \hspace{1cm} (6.1)

Which is a linear interpolation of the instrument response, being pA·s for the FID and Hz·s for the ECD. The reference concentration is a well-known value in for example ppm, the area of the sample (one could also use the height of a peak) and reference refers to the output of the detector.

Using two calibration points and two samples (RssR) the concentration can be determined by calculating its weighted average relative to the references, hence: the concentration of sample 1 is given by:

\[
\text{concentration ref.} \cdot \frac{\text{area sample 1}}{\left(\frac{1}{3} \cdot \text{area ref. 1} + \frac{1}{3} \cdot \text{area ref. 2}\right)}
\]  \hspace{1cm} (6.2)

And the concentration of sample 2 is then given by:

\[
\text{concentration ref.} \cdot \frac{\text{area sample 2}}{\left(\frac{1}{3} \cdot \text{area ref. 1} + \frac{2}{3} \cdot \text{area ref. 2}\right)}
\]  \hspace{1cm} (6.3)

This is again a linear interpolation of the detectors response at the time of the sample measured.

---

\(^{25}\) The two reference points (calibration points) are from the same cylinder with a well-known value.
The concentrations of the samples were now calibrated and their standard deviation was calculated for several calibration intervals: 1, 2, 3, 4, 5 or 6 samples between two calibration points.

Table 6.1: Determination of the optimal calibration intervals. The most upper values for CH$_4$ represent values as measured at the CO$_2$-line. The other values for CH$_4$ represent values as measured at the CO-line

<table>
<thead>
<tr>
<th>Stdev. %</th>
<th>RsR</th>
<th>RssR</th>
<th>RssssR</th>
<th>RssssssR</th>
<th>RssssssssR</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$ area</td>
<td>0.012</td>
<td>0.017</td>
<td>0.018</td>
<td>0.020</td>
<td>0.026</td>
</tr>
<tr>
<td>CO$_2$ height</td>
<td>0.015</td>
<td>0.018</td>
<td>0.019</td>
<td>0.019</td>
<td>0.024</td>
</tr>
<tr>
<td>CH$_4$ area</td>
<td>1.774</td>
<td>1.742</td>
<td>1.720</td>
<td>1.802</td>
<td>1.770</td>
</tr>
<tr>
<td>CH$_4$ height</td>
<td>0.380</td>
<td>0.377</td>
<td>0.391</td>
<td>0.401</td>
<td>0.410</td>
</tr>
<tr>
<td>CO area</td>
<td>0.948</td>
<td>1.090</td>
<td>1.198</td>
<td>1.330</td>
<td>1.334</td>
</tr>
<tr>
<td>CO height</td>
<td>0.608</td>
<td>0.732</td>
<td>0.846</td>
<td>0.971</td>
<td>1.037</td>
</tr>
<tr>
<td>CH$_4$ area</td>
<td>1.797</td>
<td>1.789</td>
<td>1.634</td>
<td>1.667</td>
<td>1.844</td>
</tr>
<tr>
<td>CH$_4$ height</td>
<td>0.502</td>
<td>0.498</td>
<td>0.452</td>
<td>0.470</td>
<td>0.517</td>
</tr>
<tr>
<td>N$_2$O area</td>
<td>0.532</td>
<td>0.566</td>
<td>0.539</td>
<td>0.528</td>
<td>0.509</td>
</tr>
<tr>
<td>N$_2$O height</td>
<td>0.504</td>
<td>0.571</td>
<td>0.542</td>
<td>0.529</td>
<td>0.560</td>
</tr>
<tr>
<td>SF$_6$ height</td>
<td>5.499</td>
<td>5.878</td>
<td>5.920</td>
<td>6.058</td>
<td>5.935</td>
</tr>
</tbody>
</table>

Although there is a lot of variation in the data, the general trend is that increasing the amount of samples between the calibration points gives more inaccuracy in the calibrated concentration of the sample. Based on this table we conclude that at this point, four samples between two calibration points is about the maximum. The CH$_4$ that is measured at the CO-line experiences a significantly higher instability than the CH$_4$ that is measured with the CO$_2$ -line. One reason is that the peak of the latter is higher and its surface larger. Also, the integration of the CH$_4$ from the CO-line suffers from a relative unstable baseline. Since this line is to be optimised for measurement of CO, and a more reliable CH$_4$ peak is given by the CO$_2$-line, no further efforts will be done to improve the CH$_4$ measurement of the CO-line.

Furthermore, the data suggests that the highest accuracy is obtained by using the height of the peaks to determine its concentration. This was however the very first test run with the GC and the possibility exists that the setup experiences some typical start-up problems, for example caused by tubing or fitting contamination or a not perfectly dried cylinder. Furthermore, these measurements represent the very first measurements with this setup and the GC was not yet fine-tuned at the time of measurements, therefore, the results presented here are most likely to be the worst case scenario.
6.2 **Measurements at Zernike**

Measurements of ambient air were done at the Zernike complex from 19 July to 20 July. The concentration values (fig. 6.12 to 6.17) were determined with two reference cylinders (7888 high span and 9946 low span). For N$_2$O and SF$_6$, no reference values were available at the time. A day-night cycle is clearly evident within the CO$_2$ and CH$_4$ data. Day-night cycles can be explained by release and uptake effects of the biosphere, change in (CH$_4$) production by bacteria, traffic and energy demand and mainly the overnight build-up under diurnal changes of the atmospheric transport conditions.

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*Figure 6.12: CO$_2$ measured at Zernike between 19/20-07-2005.*

*Figure 6.13: CH$_4$ (CO$_2$-line) measured at Zernike between 19/20-07-2005.*

*Figure 6.14: CH$_4$ (CO-line) measured at Zernike between 19/20-07-2005.*

*Figure 6.15: CO measured at Zernike between 19/20-07-2005.*

*Figure 6.16: N$_2$O measured at Zernike between 19/20-07-2005.*

*Figure 6.17: SF$_6$ measured at Zernike between 19/20-07-2005.*

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$^{26}$ Longer measurements were no more possible during this research project but will be done later.
The day-night cycles are most obvious with the CO$_2$ and CH$_4$ data. CO$_2$ and CH$_4$ experience large changes in fluxes attributed to the biosphere activity. Another contributing factor is the wind. The wind speed between 19 July and 20 July was on average 9.5 m/s. The direction of the wind during these measurements was WSW. This could also be a reason for the relative high values of the greenhouse gases.

### 6.3 Stability of the Calibration Gases

As explained in chapter 6.1, the drift of the GC is assumed to be cancelled out by measuring the calibration gases more often. We then assume that the GC is responsible for the drift, and that both of the calibration cylinders are measured in the same way, and experience the same drift. The delta between the two calibration curves (fig. 6.18) will then stay the same. However, both of the calibration cylinders can respond differently to, for example temperature, or pressure differences. Also, there could be some contamination in one of the cylinders that interferes with the measurements, or moisture when the cylinder is not dried properly. To determine the drift between the two calibration cylinders, relative to each other for the measurements of outside air at the CIO lab (Zernike, Groningen) we used the similar approach as described in chapter 6.1, except we now compared the two cylinders (7888 and 9946) to each other. The calculations were performed on data from the Zernike measurements (chapter 6.2), with a calibration interval of every four samples: RssssR.

![Figure 6.18: Illustration of stability variation between the two calibration gases.](image)

Again, we see that the CH$_4$ that is measured on the CO$_2$-line (table 6.2) has a higher uncertainty than the CH$_4$ that is measured on the CO$_2$-line. Although the setup still has to be fine-tuned, we conclude from these results that calibration of CO$_2$ gives the most accurate results when using the integrated area. For the others, calibration is the most accurate when using the height of the peaks. CH$_4$ is already within the desired target, CO$_2$ almost and CO, N$_2$O and SF$_6$ still need to be fine-tuned. We attribute a large part of the errors to start-up problems since this was the very first run of the GC.
Table 6.2: Determination of the stability of the calibration gases relative to each other. CO, N$_2$O and SF$_6$ are not yet within their desired measurement accuracy. The most upper values for CH$_4$ represent values as measured at the CO$_2$ line. The other values for CH$_4$ represent values as measured at the CO line.

<table>
<thead>
<tr>
<th></th>
<th>Ref. value</th>
<th>Output</th>
<th>Stdev.</th>
<th>Target</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$ area</td>
<td>382 ppm</td>
<td>399.14</td>
<td>0.06</td>
<td>0.05</td>
</tr>
<tr>
<td>CO$_2$ height</td>
<td>382 ppm</td>
<td>399.31</td>
<td>0.09</td>
<td>0.05</td>
</tr>
<tr>
<td>CH$_4$ area</td>
<td>1923 ppb</td>
<td>2020.61</td>
<td>1.83</td>
<td>2</td>
</tr>
<tr>
<td>CH$_4$ height</td>
<td>1923 ppb</td>
<td>2020.27</td>
<td>1.46</td>
<td>2</td>
</tr>
<tr>
<td>CO area</td>
<td>485 ppb</td>
<td>612.94</td>
<td>17.02</td>
<td>1</td>
</tr>
<tr>
<td>CO height</td>
<td>485 ppb</td>
<td>624.30</td>
<td>15.84</td>
<td>1</td>
</tr>
<tr>
<td>CH$_4$ area</td>
<td>1923 ppb</td>
<td>1963.45</td>
<td>50.64</td>
<td>2</td>
</tr>
<tr>
<td>CH$_4$ height</td>
<td>1923 ppb</td>
<td>1965.36</td>
<td>47.22</td>
<td>2</td>
</tr>
<tr>
<td>N$_2$O area</td>
<td>320 ppb</td>
<td>318.27</td>
<td>2.21</td>
<td>0.1</td>
</tr>
<tr>
<td>N$_2$O height</td>
<td>320 ppb</td>
<td>318.37</td>
<td>1.82</td>
<td>0.1</td>
</tr>
<tr>
<td>SF$_6$ area</td>
<td>6 ppt</td>
<td>7.23</td>
<td>0.82</td>
<td>0.1</td>
</tr>
<tr>
<td>SF$_6$ height</td>
<td>6 ppt</td>
<td>7.33</td>
<td>0.52</td>
<td>0.1</td>
</tr>
</tbody>
</table>

The inaccuracy is not the same for each compound, this suggests that the GC is not responsible for all of the fluctuations in the data. Besides (room) pressure and temperature changes, another cause is the changing of the freezing fingers. When installed, this new freeze finger is not immediately at freezing temperature, and it is possible that some moisture has gotten into the columns. Furthermore, the compounds measured with the ECD detector, N$_2$O and SF$_6$ depend highly on the quality of the carrier gas, especially SF$_6$ is extremely sensitive to noise, since it has a concentration in the order of less than 10 parts per trillion.

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27 In a test a few days later containing measurements from 3 days, the standard deviation for CO (height) was 4.7 ppb. This indicates that the data from this table include start-up problems.

28 Glass tube in which moisture from the sample air is frozen to dry the air before flushing the GC sample loops.
CHAPTER 7: DISCUSSION AND CONCLUSIONS

To be able to measure the atmospheric concentrations of the most important trace gases, an Agilent Hp 6890 gas chromatograph (GC) was modified and improved. This GC is being used at the limits of its capabilities. Extremely small concentrations of trace gases are being measured in a relatively large amount of molecules. Especially the Electron Capture Detector was not designed to measure sample air from the packed column with a relative high internal volume. Normally, it is used with capillary columns and only a very small amount of sample is injected. Also the flow rate that we used is extremely high. The reason for this is that we want to be able to do as many measurements as possible at the three heights at Lutjewad. One of the problems is that when using such high flow rates, the FID flame blows out when switching a valve. The problem with the FID flame was greatly improved by re-tubing the FID inlet. The repairs and adjustments that were needed for the system to work, required a lot of time, but also gave useful insights in the functioning of the device. This knowledge will be of great use with the interpretation of future data, and maintenance of the GC during future research.

The gas chromatograph was strongly improved by adding the ability to also measure carbon monoxide (CO), which like SF$_6$, can be used as a powerful tracer for determination of the origin of the greenhouse gases. At this time, we have no knowledge of existence of any similar setup in the world. The possibility of measuring CO$_2$, CH$_4$, N$_2$O, SF$_6$ and CO with only one GC is probably unique. Besides having to purchase an expensive second device, the advantages, of this method are that the various substances are measured from the same sample and under the exact same conditions, which make correlations between them more reliable.

The first test results indicate that the system experiences a significant drift. Therefore, the measurements of CO ($\pm 15.8$ ppb), N$_2$O ($\pm 1.8$ ppb) and SF$_6$ ($\pm 0.5$ ppt) are not within the desired accuracy of $\pm 1$ ppb, $\pm 0.1$ ppb and $\pm 0.1$ ppt respectively. CO$_2$ ($\pm 0.06$ ppm) was measured with a standard uncertainty of almost the target ($\pm 0.05$ ppm) and CH$_4$ ($\pm 1.46$ ppb) is measured well within the target of $\pm 2$ ppb.

These results are obtained from the very first test run with the new configuration of the gas chromatograph and fine-tuning of the setup, mostly the GC software, has to be done to get better results. A calculation on data that was measured later, indicated a standard uncertainty for CO of $\pm 4.7$ ppb$^{29}$. This is already a significant improvement and it suggests that a large part of the inaccuracy of the measurements can be attributed to start-up problems and give confidence that the desired measurement criteria will be achieved in the very near future by fine-tuning the setup.

$^{29}$ The data of these measurements could not be included in this report.
This final chapter provides some useful information for improving the setup further in the future.

First of all, the adjustments of the setup should be fine-tuned to improve measurement stability and reproducibility. Significant improvements can be achieved by optimisation of the GC software that integrates the chromatogram peaks.

The time needed for flushing the tubes and sample loops can be decreased significantly when replacing the sample inlet mass flow controller (100 ml/min) with a mass flow controller that has a maximum of 500 ml/min, which is about the maximum flow that can be achieved with this setup.

The 5 ml sample loop that is used for CH₄/CO₂ should be replaced with a loop of 10 ml. This will increase the amount of CO₂ molecules that are measured and thereby increase the precision.

At the measurement site Lutjewad, there will be also an oxygen analyzer installed at which requires the sample air to be cooled at -80°C. We suggest that this cooler will be also used for cooling the sample air for the gas chromatograph. This does not only save money, but also reduces the measurement errors due to water vapour in the sample even further.

Dependent on the position of the multivalve, valves VAO, VBO or BCO (see appendix IV) should be switched on or off in order to drain the sample air from the tower at the three different heights. This requires that the BCD code that controls the multivalve should be continuously read, and dependent on the position of the multivalve, given by the BCD code, its corresponding valve (VAO, VBO or BCO) should react. This will guarantee a continuous flow from all heights (flushes the tubing), and makes it possible to reduce the flow to zero (in order to get sample in equilibrium with the ambient pressure) without the pumps being closed at one end.
## Glossary

<table>
<thead>
<tr>
<th>Term</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aerosols</td>
<td>A collection of airborne solid or liquid particles of natural or anthropogenic origin, and residing in the atmosphere for at least several hours. Influence climate in two ways: directly through scattering and absorbing radiation, and indirectly through acting as condensation nuclei for cloud formation or modifying the optical properties and lifetime of clouds.</td>
</tr>
<tr>
<td>Calibration</td>
<td>Determination of the response of the detector for a given component with known concentration.</td>
</tr>
<tr>
<td>Chromatogram</td>
<td>The recorder chart response to an analysis of a gas air mixture.</td>
</tr>
<tr>
<td>ECD</td>
<td>Electron Capture Detector. Measures current decrease as produced by capture of electrons from a radioactive source. The amount of electrons captured depends on the amount electron accepting of molecules in the sample.</td>
</tr>
<tr>
<td>FID</td>
<td>Flame Ionisation Detector. Detects, with use a hydrogen flame, organic vapor concentrations in air.</td>
</tr>
<tr>
<td>Gas chromatograph</td>
<td>A device that separates the components in a gas.</td>
</tr>
<tr>
<td>Greenhouse gas</td>
<td>A gas, such as water vapor, carbon dioxide, methane, that absorbs and re-emits infrared radiation, warming the earth's surface and contributing to climate change.</td>
</tr>
<tr>
<td>Methanizer</td>
<td>Catalyst packed with a nickel catalyst powder. When the column effluent mixes with the FID hydrogen supply and passes through the Methanizer at 375 °C, CO and CO₂ are converted to methane.</td>
</tr>
<tr>
<td>Photolysis</td>
<td>Chemical process by which molecules are broken down into smaller units through the absorption of UV-light.</td>
</tr>
<tr>
<td>Radiative forcing</td>
<td>A change in the balance between incoming solar radiation and outgoing infrared radiation</td>
</tr>
<tr>
<td>Trace gas</td>
<td>A gas that makes up less than 1% of the earth's atmosphere. The most common trace gas is argon. Among the trace elements and compounds are the greenhouse gases.</td>
</tr>
</tbody>
</table>
REFERENCES


APPENDIX

This appendix contains:

I  Parameters and schematic design of the GC
II  GC external valve connections
III  Mass Flow Control box
IV  Schematic representation of Lutjewad Measurement site
### APPENDIX I: Parameters and schematic design of the GC

<table>
<thead>
<tr>
<th>Parameters and Design</th>
<th>Details</th>
</tr>
</thead>
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<tr>
<td><strong>General:</strong></td>
<td></td>
</tr>
<tr>
<td>Oven:</td>
<td>72 °C</td>
</tr>
<tr>
<td>Sample:</td>
<td>7 min</td>
</tr>
<tr>
<td>Valve box heaters:</td>
<td>Aux 1 and 2</td>
</tr>
<tr>
<td>Carriergas FID:</td>
<td>N&lt;sub&gt;2&lt;/sub&gt; 5.0</td>
</tr>
<tr>
<td>FID supply:</td>
<td>Air 300 ml/min</td>
</tr>
<tr>
<td>Carriergas ECD:</td>
<td>Arg/CH&lt;sub&gt;4&lt;/sub&gt; 6.0</td>
</tr>
</tbody>
</table>

| CH<sub>4</sub>/CO     |         |
| Detector:             | FID 250°C |
| Catalyst:             | Back inlet 385°C |
| Columns:              | Porapak Q 6 feet 80/100 mesh |
|                       | Molsieve 5A 4 feet 60/80 mesh |
| Carrier:              | Aux 5 (inj. & backfl.) 0-1.5 min, 65 psi 1.5-7 min, 5 psi |
| Carrier:              | Aux 3 0-3.5 min, 65 psi 3.5-7 min, 15 psi |

| CH<sub>4</sub>/CO<sub>2</sub> |         |
| Detector:               | FID 250°C |
| Catalyst:               | Back inlet 385°C |
| Column:                 | Haysep Q 10 feet, 80/100 mesh |
| Carrier:                | Aux 4 35 psi |

| N<sub>2</sub>O/SF<sub>6</sub> |         |
| Detector:                 | ECD 390°C |
| Columns:                  | Haysep Q 6 feet, 80/100 mesh |
|                           | Haysep Q 4 feet, 80/100 mesh |
| Carrier:                  | Front inlet (inj. & backfl.) 0-0.3 min, 40 ml/min 0.3-4.7 min, 90 ml/min 4.7-7 min, 40 ml/min |
| Carrier:                  | external Mass Flow Controller 80 ml/min |
A detailed description of the CO/CH4-line (upper part) and the CO2/CH4-line (lower part) of the GC.
A detailed description of the N$_2$O/SF$_6$-line of the GC.
A detailed description of the external event cable of the GC, used to control the external mass flow controllers and valves.
A detailed description of the mass flow control box that is used to control the two external mass flow controllers and the two external valves with the GC software.
A detailed description of the air inlet control at Lutjewad. The air is flushed from three different heights (7m, 40m and 60m) with 2 L/min to keep a constant flow of new sample air.