On-Line Gas Analysis Using Microwave Technology

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ABSTRACTS

Microwave technology has for decades been a tool for astronomers in their work to map and understand the complexities of the universe due to composition and extent. The technology is also frequently used on laboratory scale to examine properties of atomic and molecular compounds. Combining the knowledge gained in those these fields of research and transferring it to the environment of the Steel and metal industry, a project to investigate microwave spectroscopy for on-line process control has been launched.

Due to the fact that the dynamic in most metallurgical processes as well as combustion processes is very fast and the response time for conventional extractive gas analysers is long, off-gas analysis for on-line process control is not expedient with this technology. On the other hand, by exploiting microwave technology, its short response time and high sensitivity for gas analysis, disadvantages such as long response time could be eliminated, and thus improve the process efficiency. With this approach a process control on-line in “real time” is possible. On-line gas analysis entails an improved process control, which for metallurgical and combustion processes implies energy savings, reduced emissions of green house gases and improved productivity.

In this novel work we will present a series of trials in which a high tempered gas flow is spectroscopically analysed in a frequency band ranging from 110 to 120 GHz. The objective is to stimulate compounds sensitive to radiation in this frequency band to make a transition from one energy level to another and in doing so giving up energy that can be detected by the measuring system. Of interest for the steel and metal industry are molecular compounds such as CO, CO_2 (isotope), O_2, NO, NO_2, H_2O, OH and SO_2.

BACKGROUND

Today conventional extractive technologies for off gas analysis are frequently used in the steel and metal industry to overview furnaces and monitor environmental emissions. However due to the dynamic of a smelting process in combination with long response time, extractive technologies are not expedient for real time gas analysis and thus not for an on-line process control. In a process such as the LD process where the carbon removal rate from the melt can be directly correlated towards the amount of carbon dioxide present in the off gases, a real time analysis would mean an increased accuracy due to process termination which will lead to a shorter process time and in its extension a decrease in energy consumption and an improved production yield.

Contact free technologies such as the Tuneable Diode Laser Absorption Spectroscopy (TDLAS), is a well established technology for gas analysis. However, in metallurgical smelting processes it is less expedient due to its susceptibility to dust. The laser beam can simply not penetrate higher concentrations of dust in the off gas flow. Therefore, as an attempt to eliminate problems related to a long response time as well as high dust loads, microwave technology has been tested in a series of trials with focus on investigating the process off-gases due to the presence of specific molecular compounds and their temperature dependence. These compounds are CO, CO_2 (isotope), O_2, NO, NO_2, H_2O and OH. The trials were performed on high tempered gases in an experimental furnace by exposing the gas flow to electromagnetic radiation in a frequency band ranging from 110 to 120 GHz.

OBJECTIVES

The objectives during the trials have been to investigate the physical temperature dependence of individual molecules at different concentration levels and correlate this dependence against known microwave frequencies for these molecules. The long term objective is to use this knowledge to control a metallurgical smelting process on-line and in real time.

POSSIBLE APPLICATIONS

The LD converter process is one of many smelting processes that would benefit from a fully operational microwave technology for gas analysis. During the oxygen blow and the removal of the carbon from the steel melt, large quantities of carbon monoxide and dust are generated. The amount of carbon monoxide in the fume is a measure of the carbon concentration in the melt and thus by measuring the carbon monoxide variations in the off gases the carbon removal rate from the melt can be followed on line. Seen in a process control perspective this means an optimised blowing time and thus an improvement of the accuracy in termination of the process. This is expected to provide energy savings as well as a lowered emission of green house gases to the environment. In Figure 1 is a LD converter shown and in the figure is an indication, red dotted line, where an instrument could be mounted. At this position the instrument is as closed to the furnace it can be without becoming a part of the process.

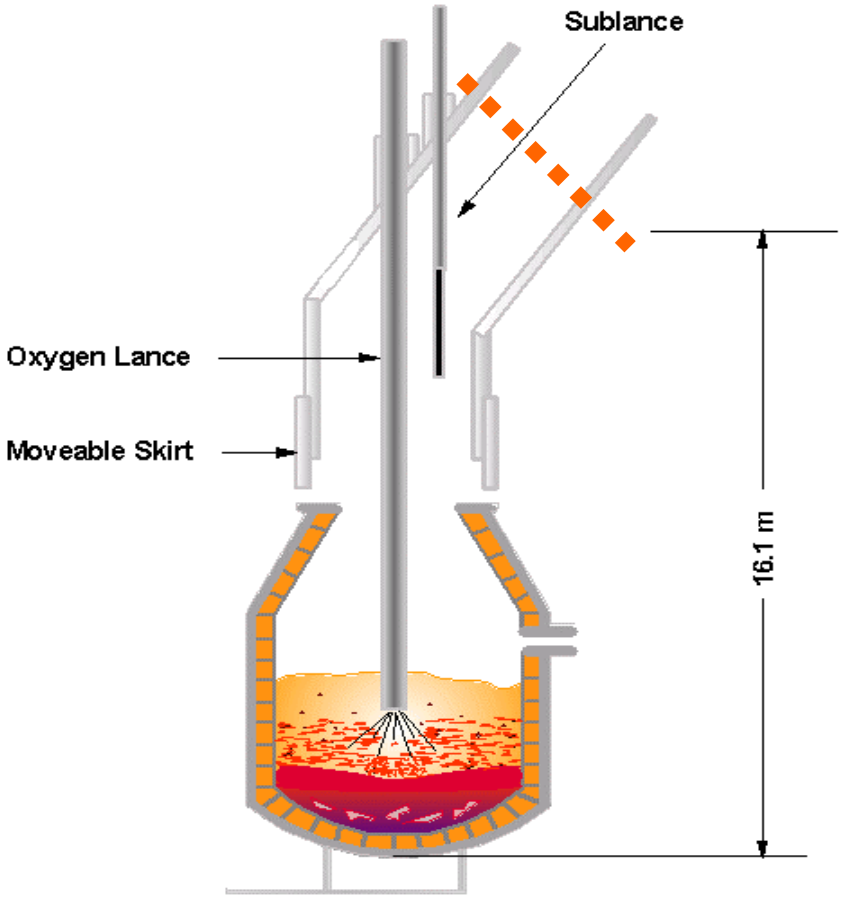

Figure 1. LD Converter

THEORETICAL APPROACH

From physics it is known that physical properties of matter are temperature and frequency dependent and that one of the most distinguished properties of electromagnetic radiation is that it can penetrate matter. Therefore changes in the pattern and polarization of electromagnetic waves represent the most sensitive probes in physics in that respect that the pattern of modulation also is representative to the matter of interest. Electromagnetic waves may propagate through matter of varying physical properties, changing their phases and amplitudes as well as their polarization in a way typical to the matter of investigation. In this respect matter of gaseous solid or liquid nature will emit or absorb electromagnetic radiation mainly depending on its composition, density, temperature, and the molecular structure as well as the electromagnetic field to which the matter is exposed. Continuum radiation will also be affected when propagating through matter as attenuation of the amplitude, as changes in the propagation velocity, but also resulting in phase alterations due to energetically favourable interactions with the molecular di-poles.

By exposing molecules in a gas to electromagnetic radiation it is possible to excite or de-excite the molecule by absorption or emission of radiation. The energy exchanges in such transitions, typical to the molecules, are measurable, and constitute a spectrum that could be called the molecules fingerprint. As a first approximation the energy of a molecule can be written as

$$E = E_{electronic} + E_{vibrational} + E_{rotational} + E_{translational} \quad (1)$$

However in microwave spectroscopy the energy part due to electronic transition can be excluded due to high energy levels normally giving rise to spectra in the UV or visible range of the electromagnetic spectrum. Transitions between vibrational levels within the same electronic state give rise to spectra in the near infrared and are called vibrational-rotational spectra. Transitions in the far infrared range and at lower frequencies arise from transitions between rotational levels and are called pure rotational spectra or microwave spectra. During a transition between two energy levels a molecule either emits or absorbs energy. These processes give rise to spectra characteristic to the molecule under investigation and can thus be identified.

In the work presented in this paper, a way to investigate the presence of molecular compounds transition pattern by stimulated emission in off gases from an experimental process will be evaluated. The investigations will be performed on high temperature gases at atmospheric pressure. In this respect, the chosen approach is novel and the focus of the work presented in the first series of trials is towards experimental performance. The theory behind microwave spectroscopy is beyond the scope of this paper and will therefore be omitted. However, for the interested Townes[1] is highly recommended.

TRIAL PERFORMANCE

The trial performance can be divided into two steps:

- The design and construction of sensors for the frequencies of interest
- Trials in an experimental furnace on gases at high temperatures and atmospheric pressure

Sensors Construction

The sensors consists of antennas and various electronic devices suitable to fit them to a signal generator making the system as a whole working within the frequency window of interest, i.e. 110-120GHz , see Figure 2. As signal generator as well as a data collecting unit during the trials, a vector network analyzer(VNA) was used. Prior to high temperature trials the sensors were evaluated on laboratory scale due to signal performance.

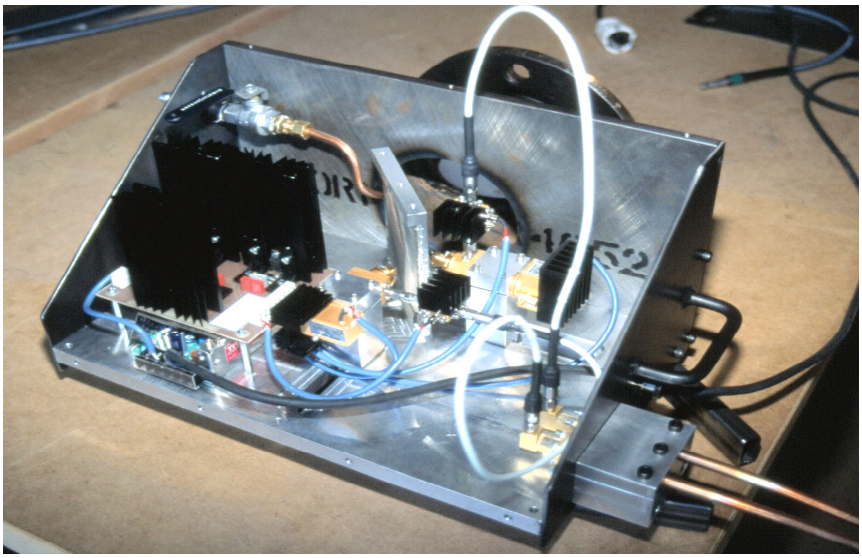

Figure 2. Microwave Sensor Mounted in Encapsulation

Pilot Trials in Experimental Furnace

The experimental pilot furnace is especially designed for trials on high temperature gases. The unique furnace design allows simulated, but still controlled production conditions, by manipulating the stoichiometric parameters during the trial performance and thus controlling the combustion performance, see Figure 3. In the figure is the measuring path marked with a red dotted line.

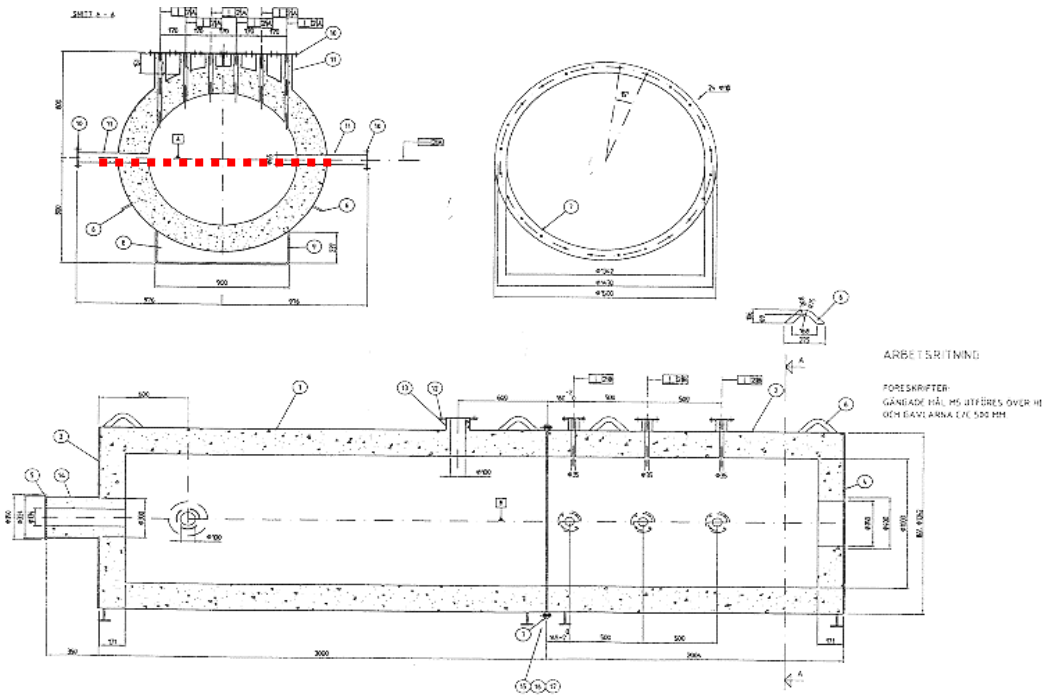

Figure 3. Drawing of Experimental Furnace

A 1 MW oxy/fuel burner was used for combustion and generation of the required furnace atmosphere. As fuel, different mixtures of oxygen, Propane, N2 and air was used to generate

the requested furnace environment. For comparative measurements, the furnace was equipped with conventional extractive gas analysers and thermocouples and the measurement data were logged to the main frame computer. The thermocouples and the analyser were mounted in the furnace so one could read off the furnace status along the microwave measuring path across the furnace volume. A trigger signals between the VNA and the main frame computer ensured the timing between the measuring systems.

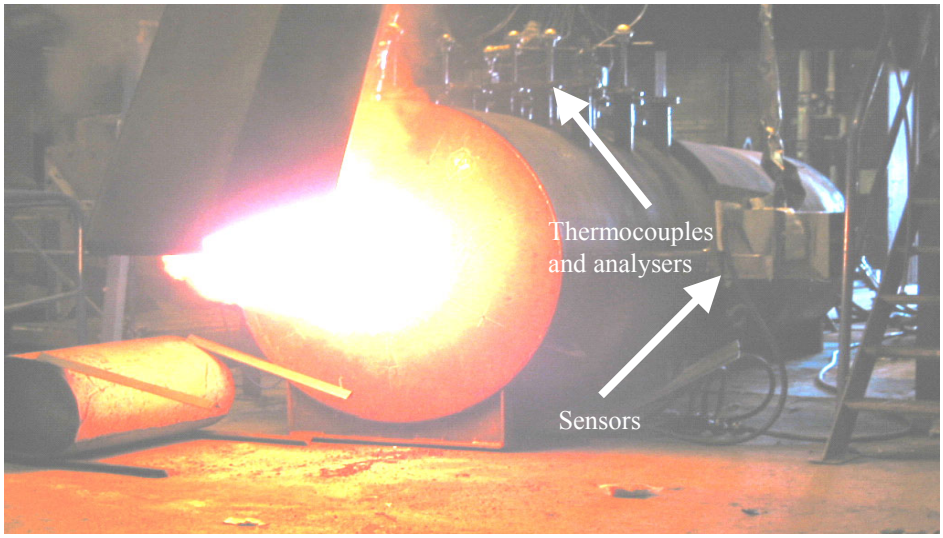

Figure 4. Experimental Furnace

The position of the sensors as well as the control equipment can bee seen in Figure 4.

Experimental Settings

The trials were performed at four different temperature levels: 1200, 1400, 1600 and 1700 ºC. At each temperature the stoichiometric conditions could be changed by varying the combustion mixture and thus the furnace environment due to the concentration levels of oxygen and carbon monoxide. This provided the necessary furnace conditions for the investigation. When the process had reached thermal equilibrium regarding temperature and concentration level the microwave measurements started. Figure 5 shows a diagram describing the expected furnace environment at 1600 ºC.

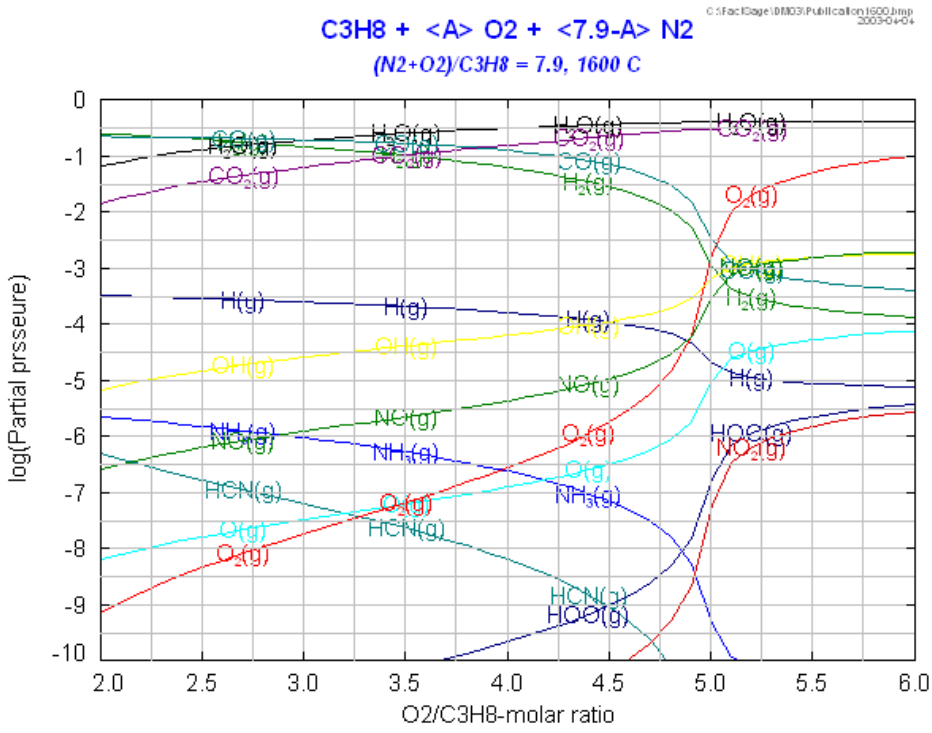

Figure 5. Thermal Equilibrium at 1600 ºC

The logarithmic scale along the ordinate gives the instantaneous compound concentration as the partial pressure during the measuring sequence. Along the abscissa is the ratio oxygen/Propane presented. By this procedure the individual levels for each of the compounds of interest can be calculated and subsequently compared with the received data for the conventional technologies in the off-line analysis of process data.

RESULTS

One metallurgical which is very interesting to control is the LD Converter process. In this respect the results presented will be focused on carbon monoxide at three different temperatures 1200, 1400 and 1600 ºC.

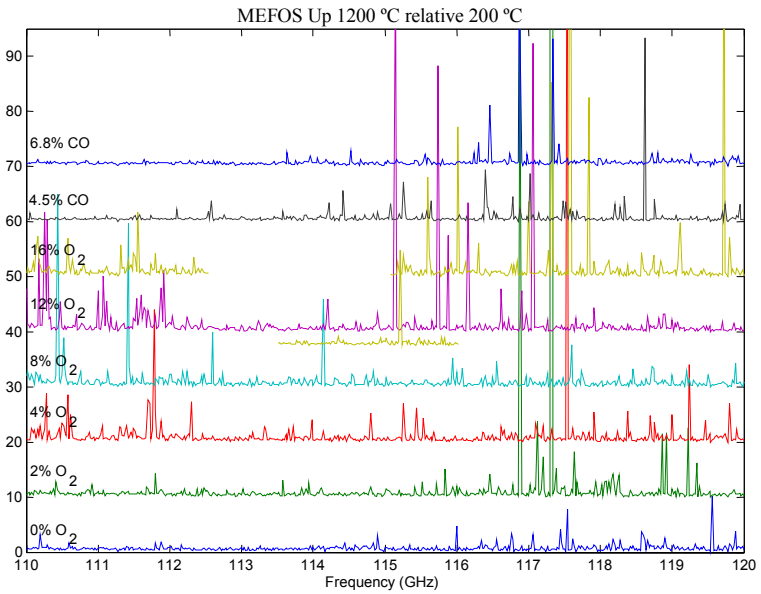

Figure 6. Gas Spectra Received at 1200 ºC for Different Molecular Mixtures

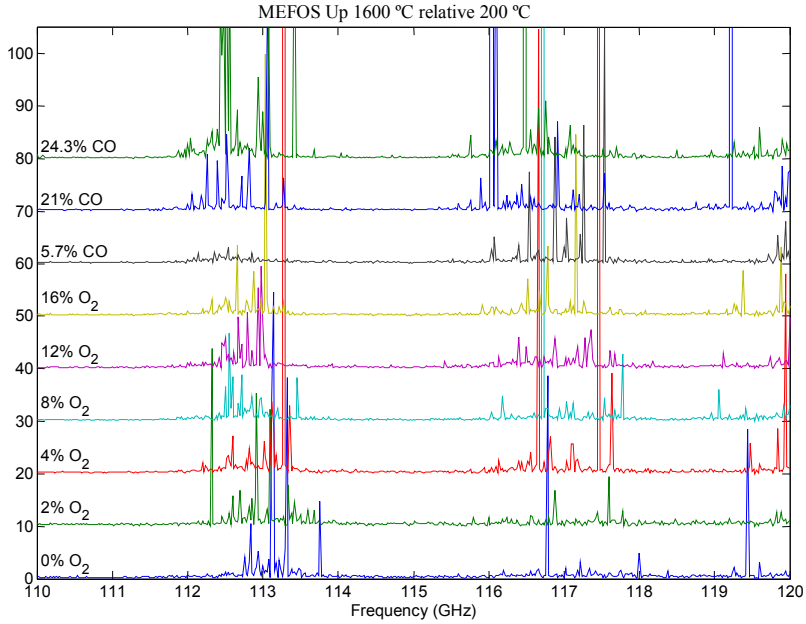

Figure 7. Gas Spectra Received at 1600 ºC for Different Molecular Mixtures

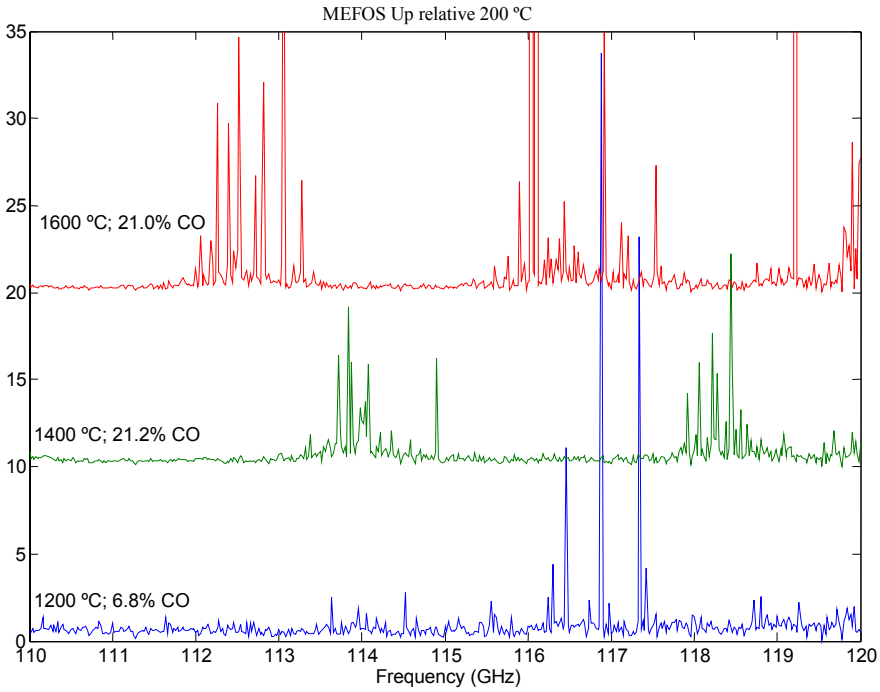

Figure 8. Gas Spectra Received for Three Different Temperatures for CO

DISCUSSION

The trials reported in this work were performed on high tempered gases at atmospheric pressure in an experimental furnace. It is a novel approach and therefore as a part of the evaluation of data, spectroscopic information regarding molecules of interest have been downloaded from JPL(JPL Catalog Search Form) and used as a guideline to find correlation between recorded data and specific molecular frequencies, see Table 1. Since the metallurgical process of interest is the LD Converter process (BOS/BOF) the focus in the evaluation is towards carbon monoxide.

Table 1. JPL frequency data for selected molecules of interest

Molecular compound	Frequency (GHz)	Single/Band
OH	113.60	Band
CO	115.27	Single
CO+	117.69	Single
	118.10	Single
C-13-O	110.20	Single
CO-17	112.36	Single
NO2	110.94	Band
	111.49	Band
	112.96	Band
	113.48	Single
	113.50	Single
	116.51	Single
	117.01	Band
	117.66	Band
	118.94	Band
	119.28	Single
	119.43	Single
NO+	119.19	Band
N2O-18	118.59	Single
O-17-CO	113.50	Single
O-18-CO	110.38	Single

In Figure 6-8 spectra are presented for three different temperature levels 1200, 1400 and 1600 ºC. Note that the different components in Figures 6-8 are presented off set to give a better overview. During the measurement, when these spectra were recorded, the only parameter that was changed was the one adjusting the concentration level of carbon monoxide. As can bee seen in Figure 6 the spectrum at 1200 ºC has a number of peaks, but with no apparent concentration. In Figure 7 however at 1600 ºC there is a strong concentration of frequency lines grouped around 113 GHz but also between 116 and 118 GHz. Figure 8 shows the apparent change of concentration with temperature for carbon monoxide.

Our experiment set-up is such that it is only sensitive to receive coherent signal from the transmitter and only attenuation or amplification of the transmitted signal is received. Our system is in-sensitive to spontaneous emitted lines since such would be in-coherent to the transmitted signal. We therefore conclude that the spectral lines observed by us are either due to absorption or stimulated emission (negative absorption).

Work is presently in progress to identify the concentration of molecular lines as seen at higher temperatures. Tentative identifications are summarized in Table 1. In addition to these, there are also vibrational exited states present. Such exited states will result in additional lines near the ones at ground state as in Table 1.

CONCLUSIONS AND FUTURE WORK

It is obvious that with the present experimental set up it is possible to detect process changes due to temperature and concentration. Work is in the progress to correlate those process changes to specific molecular compounds and especially to carbon monoxide. However is it difficult to correlate those process changes to a specific molecular compound, in this case carbon monoxide.

A new set of sensors have been designed and the assembling work has started. The operational capacity will be investigated together with new software in a series of trials that will be performed during the autumn and winter 2003. With this approach we hope that a more fundamental investigation of the spectral information will be performed.

REFERENCES

[1] Microwave Spectroscopy: C.H. Townes and A.L.Schawlow, ISBN 0-486-61798-X