

Isotopic study of CO₂ from industrial off-gases emission

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Abstract. The monitoring of greenhouse gases originating from different sources will be a crucial problem during this century. Experiments have been performed in order to obtain stable isotope composition of CO₂ emitted by large industrial off-gas emitters. A special set for sample collection in field conditions was designed and tested. Two different methods of CO₂ extraction were elaborated: vacuum extraction and extraction with carrier gas. Preliminary results of CO₂ stable isotope composition emitted from an electric power plant during one working season are presented.

Key words: greenhouse gases • stable isotopes • CO₂ anthropogenic emitters • isotope ratio mass spectrometry

Introduction

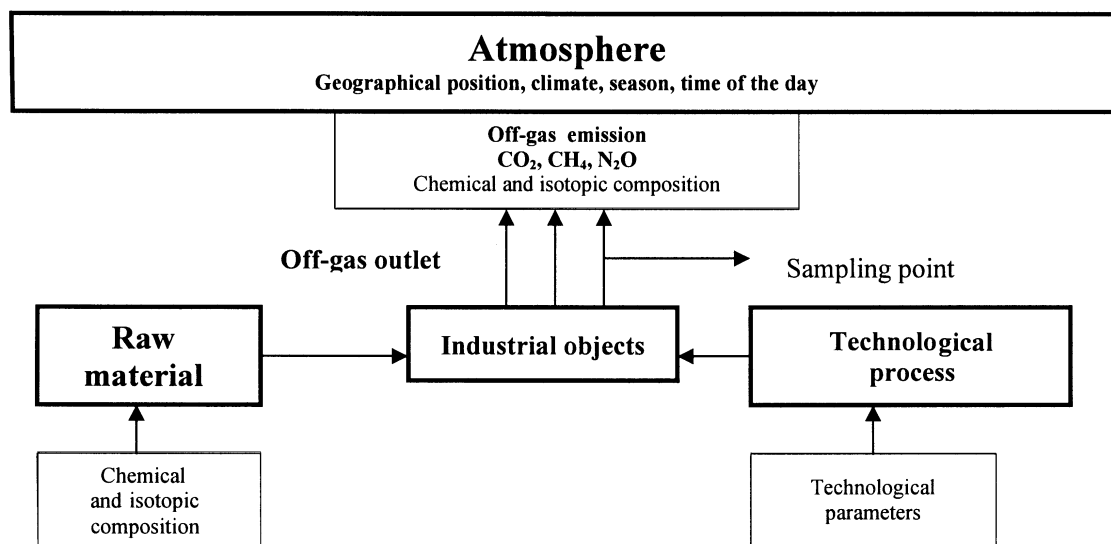
New methods of greenhouse gases control, identification and prediction of their future concentration have been recently elaborated. The isotopic methods are frequently used for greenhouse gas study. The main object of the present study is an isotopic identification of different sources of greenhouse gasses from large industrial plants which are the main stakeholders of CO₂ emission to the atmosphere (Scheme 1). Industrial objects such as a power station, an incinerator plant and a landfill located in the densely populated large urban agglomeration of the city of Warsaw were chosen as subjects of our interest. Not only the concentration and emission throughput of the emission, but also the isotopic characteristic is essential for the identification of CO₂ emission sources.

Oxygen and carbon stable isotope compositions of different ecosystem components provide a powerful tool to quantify the component in the ecosystem. When this tool is used jointly with concentration and flux measurements more information is collected [10]. Atmospheric CO₂ provides a link between biological, physical and anthropogenic processes in the ecosystem [3]. Precise knowledge of all these processes is necessary for a comprehensive understanding of the global carbon cycle [8, 9]. The present work is focused mainly on the industrial origin of carbon dioxide because of its enormous contribution to the air CO₂ budget. To calculate this contribution, an isotope ratio analysis of CO₂ emitted by different sources is important.

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Scheme 1. Schematic diagram of greenhouse gases emission from industrial objects.

Methods

Sampling

Gas samples were taken many times from a power station during one working season. In the same time, samples of coal supplied to the boiler furnace were collected. Typically, a single sample of fuel was collected from the belt loader in few minutes. The mass of the sample was about 2 kg.

To determine isotopic composition of carbon dioxide emitted from industrial processes it is important to collect a representative gas sample. A portable gas sampler for collection of off-gas samples, specially elaborated for this study, is shown in Fig. 1.

From each of the gas sampling ports, which are situated at the electrofilter outlet, the off-gases are collected in three glass vessels. Two samples are collected for isotope ratios measurement, the third one for gas chromatography analysis only during the 2009/2010 heating season. The sampling set is equipped with a small diaphragm pump (N86 KTDCB: KNF Neuberger GmbH, Germany) supplied with a battery (DC12V/7Ah). Combustion gases enter the sampler at a flow rate of 5 L/min by a probe with ceramic filters placed coaxially. When the temperature of off-gases is higher than 150°C, it is necessary to heat the probe in order to prevent water condensation on ceramic filters. Then, the collected gas flies through three dryers. The first dryer is filled with an

indicated silica gel, the second one with calcium chloride and the third like the first one with the silica gel. Collecting of one sample takes about 3 min, the time needed to flush ten times each of the glass vessel. Samples are measured within a short time after collection to prevent changes of CO₂ isotopic composition. The time of storage is not longer than 7 days.

Measurements of stable isotope compositions of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ have been carried out on an isotope ratio mass spectrometer using pure CO₂. For extraction of pure CO₂ from off-gas samples, two dedicated extraction lines [1] were constructed and tested.

CO₂ purification

Vacuum extraction line

A special vacuum extraction line for CO₂ separation from off-gases sample, displayed in Fig. 2, was elaborated. In this method carbon dioxide is separated from other gasses by slow expansion of the gas from a vessel connected to a glass vacuum line. Then, it is purified by standard cryogenic technique based on the difference in freezing temperature of the collected gases. A vacuum pumping system placed at the end of the line forces the gas to pass through the line. Initially, the vessel with the sample is connected to the vacuum line via an *o*-ring and the line is evacuated to 10⁻⁴ mbar. The gas from the

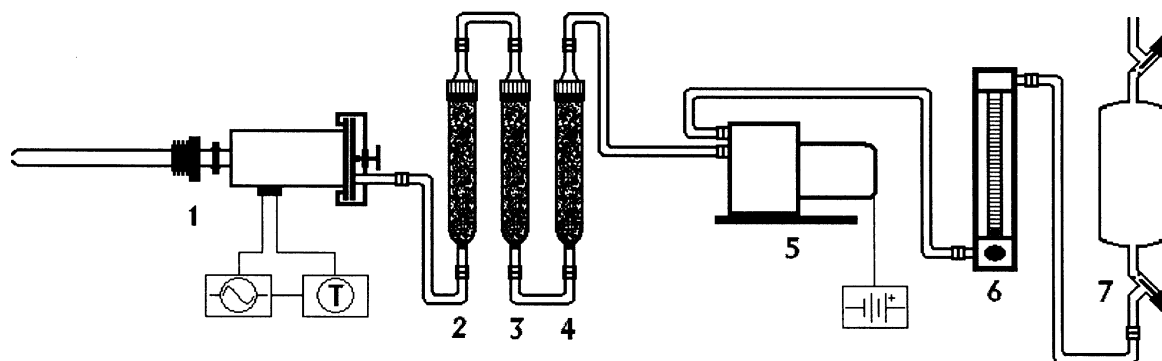


Fig. 1. Portable gas sampler: 1 – heated probe; 2, 3, 4 – dryers; 5 – diaphragm pump; 6 – flow meter; 7 – gas vessel.

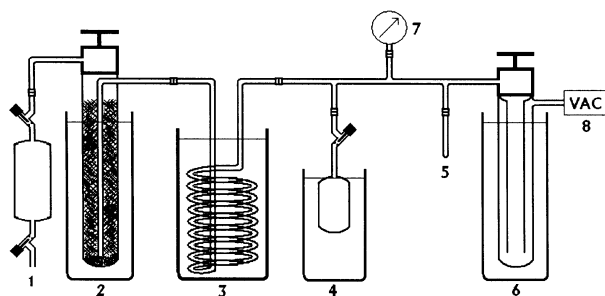


Fig. 2. Vacuum extraction line: 1 – vessel with off-gas sample; 2 – water trap; 3 – CO₂ trap; 4 – CO₂ vessel; 5 – free connector; 6 – cold trap; 7 – vacuum meter; 8 – vacuum pump.

vessel is transferred to the line and condensable compounds are collected in cold traps. Gas flow rate through the line is regulated by the vacuum valve installed on the vessel. The line consists of two cold traps. The first trap dipped in acetone chilled by LN₂ to a temperature of $-70 \pm 3^\circ\text{C}$ is designed for H₂O freezing. This trap is filled with small glass tube pieces.

The second spiral trap for freezing CO₂ is cooled by liquid nitrogen. Non-condensable gases are pumped away. At the end of the process, carbon dioxide sublimated from the second trap is cryogenically collected in a special (4) vessel connected to the line. Subsequently, the test-vessel removed from the line is connected to the isotope ratio mass spectrometer for measurement of the extracted CO₂ isotopic composition.

Continuous extraction line

A continuous extraction line has been constructed as an alternative for a vacuum extraction line. Carbon dioxide extraction process, similarly as in the vacuum line, relies on cryogenic separation of CO₂ from the off-gas sample. The main parts of the line (Fig. 3) are two spiral traps which work in the same way as in previous vacuum extraction line. The second CO₂ trap is equipped with vacuum-valves with *o*-ring connection to the spectrometer. Glass elements of the line are joined by PVC-tubes. After glass vessel connection to the line, the line is flushed ten times with helium (carrier gas) from the cylinder at a rate of 1 L/min through a by-pass installed on the vessel. In the second step, the flow rate is reduced to 40 ml/min, the sample vessel is opened and the whole line is flushed ten times. H₂O and CO₂ are collected in the cold traps. Non-condensable

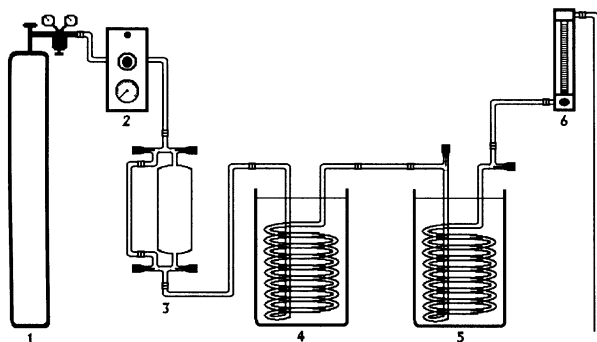


Fig. 3. Continuous extraction line: 1 – gas cylinder with carrier-gas (helium 99.9995%); 2 – pressure controller; 3 – gas vessel with by-pass; 4 – spiral water trap; 5 – spiral CO₂ trap; 6 – flow meter.



Fig. 4. Sampling point.

gases are flushed away. At the end of preparation, before the isotopic composition of CO₂ measurement, helium is pumped out from the CO₂-trap-vessel.

Results and discussion

Two or three samples were collected in one sampling session from one sampling point of off-gases installation (Fig. 4). Due to organization reasons, it was possible to take samples only from two boilers for one measurement day. The fuel for a fluidized boiler contains the biomass which is composed of wood pieces. The composition was not very homogenous. In the laboratory, each sample of fuel was dried, grinded and homogenized. Then, the measurement of carbon isotopic composition was performed by the use of an elemental analyzer connected to mass spectrometer. The results of measurement of coal isotopic composition are listed in Table 1.

The first results of stable isotope composition measurements of CO₂ from a power station were collected during the 2008/2009 heating season. The samples from two kinds of boilers were collected. After short time (2–3 days), CO₂ was extracted for comparison using two methods of extraction. Gas samples of pure CO₂ were measured by the use of Delta^{plus} (ThermoFinnigan, Germany) mass spectrometer. The preliminary results are presented in Table 1.

Conclusions

The main object of this study was to elaborate an isotopic method of analyzing greenhouse gases emission from different industrial sources. The method was used to evaluate a relation between the isotopic composition of CO₂ off-gases and the adopted technological process. Some technological parameters were collected in Table 2. Another object of this study is the examination of isotopic parameters time variability which is important for the monitoring of greenhouse gas sources.

An important result of the project is expected, namely the creation of a data base for isotopic identification of basic CO₂ industrial sources. All the information included in this data base will be used to prepare an isotopic model of industrial greenhouse gases emission which will illustrate the potential of the isotopic method

Table 1. The isotopic results for the off-gases sampling sessions – winter 2008/2009 (Power Station, Warsaw)

Date of sampling	Boiler	Fuel	CO ₂		Fuel δ ¹³ C vs. PDB (‰) ±0.05‰
			δ ¹³ C vs. PDB (‰) ±0.20‰	δ ¹⁸ C vs. PDB (‰) ±0.20‰	
27/11/2008	Classical no. 2	Coal (powder)	-24.06	-9.97	
04/12/2008	Classical no. 3	Coal (powder)	-24.03	-12.22	-23.61
	Fluidized bed boiler (A)	Coal (80%) + biomass (20%)	-24.04	-9.73	
17/02/2009	Classical no. 3	Coal (powder)	-24.38	-9.02	-23.92
	Classical no. 4	Coal (powder)	-24.22	-9.04	
17/03/2009	Classical no. 2	Coal (powder)	-24.05	-10.00	-23.69
	Classical no. 1	Coal (powder)	-24.14	-9.01	
31/03/2009	Fluidized bed boiler (A)	Coal (80%) + biomass (20%)	-24.32	-10.74	-23.82
03/04/2009	Fluidized bed boiler (A)	Coal (80%) + biomass (20%)	-24.99	-9.93	-23.96
	Fluidized bed boiler (B)	Coal (80%) + biomass (20%)	-24.40	-9.64	

Table 2. Technological parameters for a classical (powder) boiler and for a boiler with fluidized bed – winter 2008/2009 (Power Station, Warsaw)

Boiler type and no.	Off-gases temperature (°C)	Steam temperature (°C)	Steam output (T/h)	Off-gases (vol%)	Date
Classic 1	154	502	216	4.3	27/11/2008
Classic 2	163	507	209	3.5	27/11/2008
Fluid A	164	511	445	3.9	04/12/2008
Classic 3	168	505	212	2.6	04/12/2008
Classic 3	157	503	202	4.0	17/02/2009
Classic 4	174	507	210	6.4	17/02/2009
Classic 1	164	506	225	4.0	17/03/2009
Classic 2	160	505	162	4.5	17/03/2009
Fluid B	133	509	376	3.3	31/03/2009
Fluid B	138	508	374	3.2	31/03/2009
Fluid A	179	510	277	5.4	03/04/2009
Fluid B	135	509	256	4.5	03/04/2009

as a tool for anthropogenic CO₂ emission control [2, 4–7]. Studies and monitoring of some selected industrial objects are being continued.

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