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RADIOCARBON ^{14}C METHOD AS USEFUL TOOL FOR FLUE GAS MONITORING APPLICATION: REVIEW

Michał STACHÓW*

Faculty of Chemistry, University of Opole, Oleska 48, 45-052 Opole, Poland

Abstract: Cosmic-ray research which started just after the second world war in 1947, encouraged widespread use of radioactive particles in many areas of science and technology, starting from astronomy, chemistry, archaeology, biology, botany, medicine and lately ending with environmental studies. Method based on measurements of the radioactive elements remains in various samples (solid, liquid and gaseous) can be very useful tool for ecological and environmental analytical measurements. The ^{14}C liquid scintillating counting method was used for simplified determination of the biomass content in flue gas from combustion processes or in the finished bio-product. Review of the latest results and progress in this research area shows the growth of interest from industrial sector in normalised method for biomass content determination.

Key words: flue gas, monitoring, ^{14}C, radiocarbon.

1. Introduction

Determination of natural abundance of various radioactive nuclides was starting point for further space exploration in 1947 (Anderson et al., 1947; Grosse & Libby, 1947). In the next year Calvin (1948) used radioisotope labelling as a method for determination of the reaction path. From this point widespread use of "radio-chemistry" has begun in many fields of science and technology, starting from radio-astronomy, chemistry, archaeology, biochemistry, entomology, botanic, medicine and ending with ecology as well as environmental analytics studies.

One of the most popular radio-isotopes is ^{14}C carbon. It has been used for various purposes for over sixty years. For example, not only age determination (Libby et al., 1949) but also differentiation biogenic and fossil carbon content in atmosphere were performed from late 50's (Clayton et al., 1955; Currie et al., 1994), as well as food processing and analysis (Simon et al., 1968).

Industrial revolution of the nineteenth and twentieth century provided significant progress in the field of human influence on the climate change globally, particular the greenhouse gases (UE, 2007; Bogner et al., 2008). Instant growth of goods and energy consumption is correlated to the operation of fossil fuels. Most of them are utilised in various combustion processes which leads to significant CO_2 production. This particular CO_2 gain is not included in natural environmental cycle of carbon element. Of course, greenhouse gases are responsible for global warming effect that provided suitable conditions for life expansion. However, global as well as local ecosystems have their own capacity for those gases and pollutants concentrations. That is why they should be in particular interest for future generations.

In last three decades a lot of non-profit activist and political organizations where founded to put emphasis on the controlling of the global pollutant concentrations. Those actions resulted in emission restrictions in several countries for each sector of the economy. It has been one of the most important topics in legislative discussion in European Union since early 2000's (EU, 2003; Ryan et al., 2006). New eco-legislation initiatives challenges science and industry in many fields.

Fossil fuels (coal, gas, oil) which are millions of years old do not contain measurable quantities of ^{14}C radio-isotope which has 5730 years of half-life time. In contrary samples of natural resources from living organisms and those not older than two hundred years can be measured with radio-carbon method. Biomass used for combustion process is one of preferred renewable resources and does not implicate the balance of the carbon natural eco-cycle (Bogner et al., 2008).

2. Interest of ^{14}C isotope in science

Scientists have used ^{14}C isotope since the late 40's (Anderson et al., 1947; Grosse & Libby, 1947; Calvin, 1948) for many purposes. In Figure 1A the increase of interest of research activity including radio-carbon concentration measurements in last twelve years is shown. This significant rise can be explained due to the general

* Autor odpowiedzialny za korespondencję. E-mail: michal.stachow@gmail.com

scientific progress, constant hardware development and finding new niches of science interested in radio-carbon measurements. Furthermore, each year approximately 500 scientific papers are “produced” on radio-carbon topic.

Biogenic carbon concentration in various samples is one of the niches for ^{14}C concentration measurements (Rethemeyer et al., 2005) (Fig. 1B). Biogenic CO_2 from combustion processes is also in particular interest of science because of biomass combustion in power plants (Fig. 1B). However, there have been very few papers on biogenic CO_2 concentration in flue gas from real scale production and combustion plants so far.

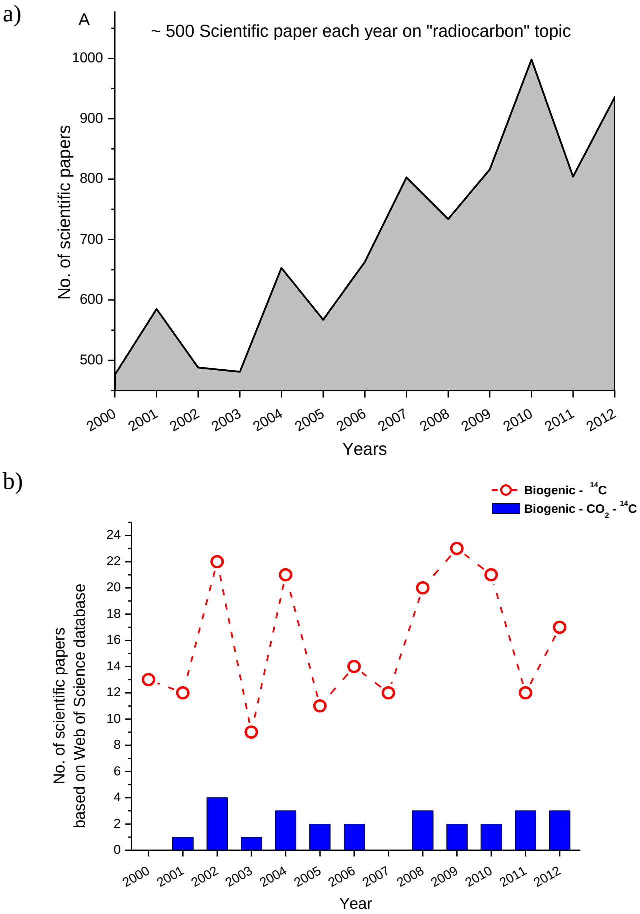

Figure 1.Amonth of radio-carbon in 2000-2012: a) general, b) biogenic radio-carbon. All statistical data taken from Web of Science database.

In Table 1 ten most interested in radio-carbon technique for biogenic CO_2 measurements scientific fields are shown. In the first place we observe particular interest of environmental sciences (Gramling et al., 2003; Rethemeyer et al., 2005; Reddy et al., 2008; Camilli et al., 2010; Joye et al., 2011; Aeppli et al., 2012), in contrary research connected to the geology as well those including bio-products (Tachibana et al., 2010). Presented results should not be interpreted in terms of absolute values but in terms of trends in scientific field.

Table 1. Interest for biogenic CO_2 ^{14}C research in different areas of science. All statistical data taken from Web of Science database.

No.	Research area	(%) of total scientific papers
1	Environmental studies, ecology	43.2
2	Geology	27.0
3	Meteorology	21.6
4	Engineering	13.5
5	Geophysics, geochemistry	13.5
6	Agriculture	8.11
7	Marine biology	8.11
8	Biotechnology – applic. Microbiology	5.41
9	Energy resources	5.41
10	Instrumental techniques	5.41

Analysis clearly shows that radio-carbon method for determination of ^{14}C concentration is mostly popular in age determination. Biogenic carbon in environmental samples are one of the niche which is slowly developing.

3. Methodology of ^{14}C measurements

The method of radio-carbon content determination is based on principle that all biogenic environmental samples are younger than 200 years and contain enough ^{14}C isotope for precise measurements. It was originally developed over twenty five years ago by Beta Analytic Inc., a well experienced in radio-isotopic area American company. Nowadays, ASTM standard prepared by them is often used (ASTM D6866-08, 2008). It is based on determination of the ratio between ^{14}C and ^{13}C isotopes (Narayan, 2006) and after that sample is crosschecked with reference sample of oxalic acid. After the measurements biogenic carbon content is calculated from equations presented below:

$$^{14}As = {}^{14}C / {}^{13}Csample \quad (1)$$

$$^{14}Ar = {}^{14}C / {}^{13}Creference \quad (2)$$

$$\Delta^{14}C = [({}^{14}As - {}^{14}Ar) / {}^{14}Ar] \times 1000\ (\%) \quad (3)$$

$$pMC = \Delta^{14}C / 10 + 100\ (\%) \quad (4)$$

where: $\Delta^{14}C$ – difference of quantitative relation between sample and reference, pMC – (percentage Modern Carbon) – content of biogenic carbon obtained from reference oxalic acid enriched with radio-carbon isotope and measured sample. For fossil samples pMC = 0%, and for biogenic carbon from photosynthesis pMC = 108-110%.

Nowadays radio-carbon analysis is performed under various analytical approaches (CEN/TR15591, 2007), however the most popular and gaining one is liquid scintillation counting (LSC). It is based on nuclear radiation detection resulting in decomposition of the unstable isotope ^{14}C to determine its concentration. Another widely used technique, that can measure the concentration of ^{14}C is the accelerator mass spectrometry (AMS) (Calcagnile et al., 2011). It is mass spectrometry using a high potential electrostatic field. The analysis is based on the direct counting of ^{14}C atoms, which are converted into a beam of ions detected by the detector. This method allows the direct ^{14}C concentration measurements.

4. Biogenic carbon in industrial flue gas studies

Quantitative determination of biogenic (from biomass) CO_2 emission level from the combustion process using ^{14}C method is well known and it has been successfully used in recent years (Fellner et al., 2007; Mohn et al., 2008; Reinhardt et al., 2008; Staber et al., 2008;). However industrial application of this method carries many question and related legal consequences that require a proper standardisation of this technique. The first attempt to this was preparation of the U.S.A. standard in 2008 (ASTM D6866-08, 2008). Different conditions and proper validation of the method with crosschecking obtained results was performed lately by Palstra and Meijer (Palstra & Meijer, 2010) in Dutch combustion installation. They used LSC and AMS method for ^{14}C determination as well as biogenic CO_2 level.

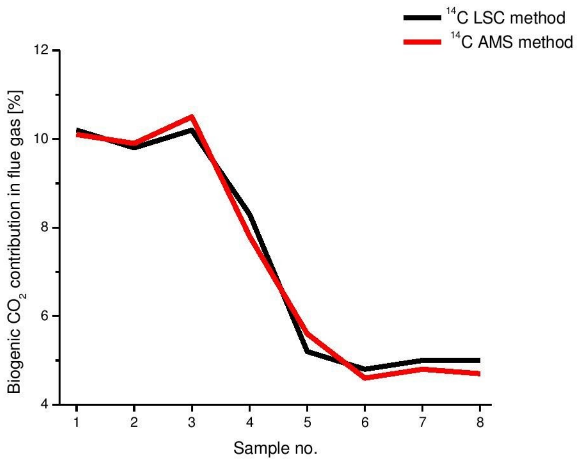

Figure 2. Comparison of LSC and AMS methods for biogenic CO_2 determination from flue gas sample obtained from combustion chimney (Palstra & Meijer, 2010).

In Figure 2 a comparison of the percentage of biogenic CO_2 fraction in power plant flue gas obtained with two ^{14}C methods (LSC and AMS) was presented. The obtained AMS and LSC results are matching.

Another example of using the ^{14}C method for determination of the biogenic CO_2 from the flue gas was carried out from three plants located in the northern part of Italy (Calcagnile et al., 2011). The calculated fbiogas were 107.17±0.84 pMC. For selected samples, the measured concentration of ^{14}C fully confirms the biogenic origin of adsorbed gas.

5. Biomass consumption in Europe

According to the EU policy for the European energy sector each country is committed to a gradual reduction in CO_2 emission (EU, 2003), replacing outdated technologies and increasing the share of renewable energy sources (Johansson et al., 1993; Swisher & Wilson, 1993; Thran et al., 2010). The main goal for EU is to achieve by 2020 level of 20%, both for emission reduction as well as for the share of so called "green technologies" (Commission, 2010).

Figure 3 shows the increase of renewable energy share in total energy consumption for EU countries based on annual basis from 1990 to 2009. Planned 12% of share in 2012, which has not been completed so far and furthermore 20% for 2020, seems to be difficult to achieve due to the hard economical conditions in Europe (Commission, 2010).

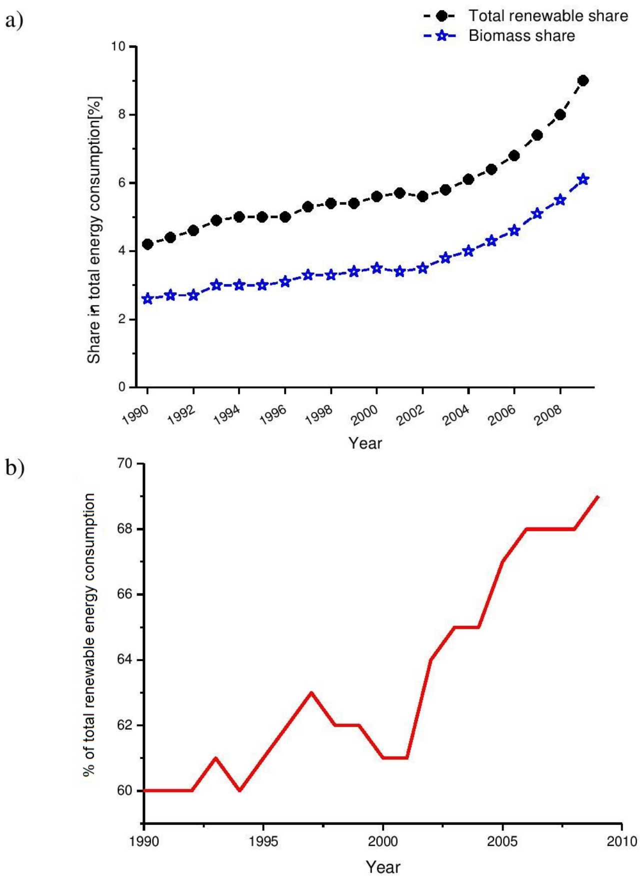

Figure 3. Renewable resources general and only biomass energy share in total energy consumption (A) and share of biomass in all renewable resources market (B). All data taken for EU (Agency 2013).

Intense scientific investigation on application of biomass in various industrial applications took place in recent years (Fujino et al., 1999; Bridgwater, 2003; Siemons et al., 2004; Aranda Usón et al., 2013). From the EU statistics the increasing share of biomass market for energy production can be observed (Fig. 3) (Agency, 2013). It is worth mentioning that the annual differences are small, although the growth rate of the "green technologies" involvement (Agency, 2013) in the energy market accelerated in the last 10 years. Despite world economic crisis, forecasts for industrial application of biomass on the market are optimistic (Hall & House, 1995; Berndes, 2003; Hoogwijk, 2003; van Dam et al., 2007; Panoutsou et al., 2009; Commission, 2010). Latest estimated results for biomass market to 2030 shows the annual several percent growth (Bentsen & Felby, 2012).

One of the major application of biomass is the industrial combustion in power plants (Calcagnile et al., 2011). It is obvious that its preferable position in "green-tech" portfolio is due to its easy application and cyclic as well as fairly quick regeneration of the resources. Today biomass use in total renewable resource technologies currently in use is up to 70% in year 2010 (Fig. 3B). Nowadays biomass can be applied even in cement industry for combustion (Aranda Usón et al., 2013; Skytte et al., 2006). Due to the limitations of CO_2 emissions and growing application of biomass as fuel it is important to evaluate the share of renewable CO_2 in total emission.

6. Summary

The ^{14}C radio-carbon method (as the content of biogenic carbon during the combustion of alternative fuels) is a very useful tool to study environmental samples, biocompatible products as well as the content of biogenic carbon during the combustion of biomass. Growing political and legislative pressure in countries like China, Australia, USA and Japan, are forcing those to initiate similar to EU control and trading systems of CO_2 emissions. This will effect with full analytical control of pollution levels. Radio-carbon method provides unique opportunity for quantitative evaluation of biogenic and fossil CO_2 concentration in flue gas.

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