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Laser based detection of $^{14}CO_2$ in radioactive waste

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Summary. — A laser based spectroscopic technology, named SCAR (Saturated-absorption CAvity Ring-down), has been demonstrated for accurate radiocarbon (^{14}C) determination in carbon dioxide. In particular, different materials from nuclear power plants, *e.g.*, concrete and graphite, were burnt and the combustion-produced carbon dioxide was analyzed to asses the amount of ^{14}C, a key species for nuclear decommissioning. The SCAR technology has demonstrated a performance equivalent or better to AMS and it is ready for further studies and deployment in nuclear waste management areas.

1. – Introduction

Radioactive waste management refers to the safe treatment, storage and disposal of liquid, solid and gas discharge from nuclear industry operations with the objective of protecting both living organisms and the environment. The anthropogenic production of radioactive waste results from medical and industrial activities, but the nuclear energy field is the most relevant source, due to the large amount of volumes generated and their

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long-lived nature. Many countries worldwide have currently active nuclear power plants (NPPs) and/or are considering the construction of new ones, while some other countries have decided to reduce or completely interrupt the nuclear energy production. This is mainly a consequence of the "double face" of nuclear energy: if it is true that the nuclear energy production is a possible way to address the climate change since it is mainly carbon free, the large volume of radioactive waste produced during the operation of NPPs raises the question about the long-term management, disposal and security issues of nuclear waste. For these reasons there is still a long debate about the sustainability of nuclear energy, especially for the long term.

The implementation of a nuclear waste disposal and decommissioning system, regardless if it is a short-/intermediate- or long-term, requires accurate determination of all the radioactive elements contained in every specific waste. An accurate radionuclides inventory allows for a secure engineering of the waste repository barrier system. Notwithstanding most of the radioactive species contained in NPP waste are in a sufficient concentration or are suited to be detected and measured by gamma spectroscopy, some of the leftover radionuclides are very or extremely difficult to be measured directly. In particular, the so called difficult-to-measure (DTM) species are a group of radionuclides characterized by pure soft alpha/beta emitters (no gamma ray) with a long half-life (often with half-lives of several thousand years) and a low penetrating power. Among this group we can find ^{14}C, ^{36}Cl, ^{90}Sr, ^{107}Pd.

The radiocarbon is a long-lived radioisotope with half-life of 5700(30) years [1]. Its atmospheric concentration equilibrium is altered by human activity by means of nuclear weapons and NPPs. In a nuclear reactor, the ^{14}C production is triggered by neutron-mediated reactions mainly involving some specific isotopes of nitrogen, oxygen and carbon, in particular ^{14}N, ^{17}O and ^{13}C [2, 3]. These target elements are present in the NPPs core, such as in graphite moderator, cooling water and air bubbles trapped in the different materials, making the ^{14}C present in a large variety of nuclear waste. ^{14}C is also a very interesting isotope because it belongs to the so-called dose-relevant radionuclides, *i.e.* nuclides that in case of uncontrolled release would have a high radiological impact in terms of dose delivered to living organisms and to the environment [4]. This is mainly due to the chemistry of radiocarbon-bearing molecules such as CO_2 or CH_4: being them very volatile and non-reactive they can migrate from the storing site, disperse in the atmosphere and be uptaken by living organisms (mainly plants or animals). Although the radioactivity related to ^{14}C is just a limited part of the overall nuclear waste activity, if we consider an apocalyptic scenario in which all radionuclides from disposal facilities and NPPs would be released, a major contribution to the total dose is associated to ^{14}C [5, 6].

These considerations pose the ^{14}C in the high-priority list of nuclides that need to be accurately measured for the design of a proper disposal site. The measurement approaches aiming to quantify the ^{14}C concentration in nuclear waste can be divided in two categories: indirect and direct ones. The most common method to determine the ^{14}C content is an indirect method that uses the scaling factors [7], defined as the ratio between ^{14}C and one or more specific easy-to-measure radionuclides. The scaling factor used for ^{14}C targets the ^{60}Co isotope. An analogous approach relies on the ^{14}C content determination from the knowledge of nitrogen impurities concentration and NPP neutron flux history. Both these methods often end up in very large uncertainties and sometimes incompatible results [8]. On the other side, direct measurement approaches mainly rely on accelerator mass spectrometry (AMS) or liquid scintillation counting (LSC). AMS is the gold standard for low-abundance isotope quantification but its availability is very limited, having only a few instruments in the developed countries. It can reach 0.002 $F^{14}C$(1) limit of detection for a typical sample with $0.1 - 1$ mg of C [9]. LSC has a similar precision, it is a much cheaper and user-friendly technology than AMS, but it requires a few grams of C to be dissolved in the scintillation cocktail.

In this paper we show that laser based saturated-absorption cavity ring-down (SCAR) spectroscopy represents a mature and valid alternative for the ^{14}C content quantification in nuclear waste. This optical approach can reach precision of 0.004 $F^{14}C$ for the analysis of a material with a few mg of C, in a very compact and small footprint instrument [10], thus proving that is a real competitor for AMS or LSC, overcoming their main limitations. In the following we will show how to measure the ^{14}C content of two nuclear disposal relevant materials: concrete and graphite originated from nuclear installation. The concrete is an example of large volume nuclear waste material, with an expected ^{14}C content which is usually in the modern or sub-modern range. In case ^{14}C and other radionuclides content would be below the clearance exemption limits (about 4 $F^{14}C$ for ^{14}C) [11], the concrete could be disposed as conventional waste, thus avoiding its storage in nuclear waste disposal sites, with a remarkable economic impact on the overall decommissioning cost. In addition, to prove the SCAR capabilities in terms of accessible measurement range, neutron irradiated graphite samples were measured. In this case, the expected ^{14}C content can span from nearly zero to hundreds of kBq g^{-1} [12].

2. – Experimental methods

One sample of concrete (identified as KB in the following sections) an two samples of graphite (from different bricks, identified as KG1 and KG2) were collected at the European Commission JRC site located in Ispra (Italy) from two different nuclear installations currently under decommissioning [13,14]. A fine powder was produced from both sample types by ball-milling them with agate spheres and the concrete sample, as it was less homogeneous, underwent an additional sieving step (below 100 μm). Two replicas of 1 g each were prepared for all samples, one to be used for AMS measurements and one for SCAR.

^{14}C mole fraction analyses were performed after the carbon content of the initial samples was converted to CO_2, a carbon compound that is suitable for both the SCAR and AMS techniques. In both cases the oxidation was done using elemental analyzers (known not to introduce any isotopic fractionation bias) that combusted the input material at high temperature in a pure oxygen atmosphere. The SCAR spectrometer requires at least 0.5 mmol of highly-pure CO_2 in order to achieve its best precision. Therefore for each sample a proper amount must be weighted and burnt, depending on its specific carbon content, in order to satisfy this requirement.

The ^{14}C mole fraction determination of the three samples was outsourced to the University of Cologne, hosting an AMS system with a gas phase ion source achieving 1% precision for a sample with 1 $F^{14}C$ mole fraction [15]. A preliminary estimation of the ^{14}C mole fraction range for all three samples was obtained with the SCAR method. This was required for AMS analyses, since toot highly enriched samples must undergo a dilution to avoid a contamination of the accelerator. The KG2 sample, which resulted

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(1) 1 $F^{14}C$, or modern, corresponds to the ^{14}C mole fraction in a natural C sample collected in 1950 having a specific activity of 0.226 Bq/g. Combining this value with the half-life of 5700(30) years [1], the obtained modern mole fraction is 1.169(6) ppt.

Fig. 1. – The SCAR spectrometer.

to be in the tens of $F^{14}C$ range, was diluted in solid forms adding a precise amount of fossil graphite with no ^{14}C. For each sample, 10 replicas (10 mg and 0.1 mg each for concrete and graphite, respectively) were combusted and independently measured after an instrument blank run and a suitable calibration were performed.

A picture of the the SCAR spectrometer, located at CNR-INO laboratory in Florence and used for these measurements [10, 16, 17], is shown in fig. 1. Any measurement based on SCAR spectroscopy starts by coupling laser light to a high-finesse two-mirror optical cavity up to a threshold level in the transmitted power. Afterwards, the laser beam is quickly switched off. An infrared photodiode detects the transmitted light during the ring-down process and the decay rate is measured. The empty-cavity loss rate (only due to mirror non-perfect reflectivity) is increased by any radiation-absorbing gas species inside the cavity and such variation is measured. Differently from conventional CRD spectroscopy, saturation effects on the molecular absorption induce a deviation of the ring-down signal from a perfectly exponential behavior, as expected for linear intra-cavity losses. Transient effects due to a changing saturation level are taken into account by a fitting routine that was developed according to a *ab initio* theoretical model: from each single CRD decay event both the empty-cavity and the gas-induced losses are retrieved [10].

The profile of the $(00^01 - 00^00)$ P(20) ro-vibrational transition of $^{14}CO_2$ at 2209.1077 cm^{-1} is recorded with high spectral fidelity by scanning the cavity frequency

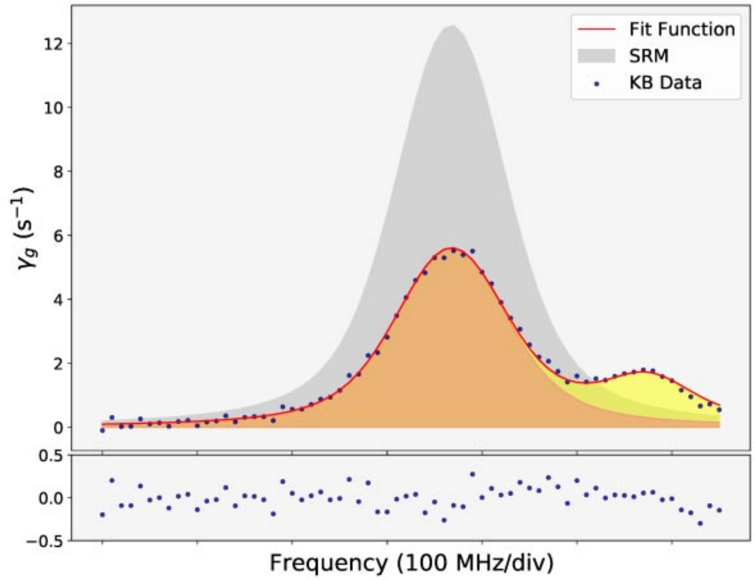

Fig. 2. – Average spectrum of the P(20) line of $^{14}CO_2$ measured for the KB sample with the interfering line of N_2O yellow shaded to the right and the line of the SRM grey shaded in the background. The ^{14}C mole fraction retrieved by fitting data to a two-line manifold Voigt profile is 0.593(8) $F^{14}C$.

and the mole fraction of this isotopologue is determined by measuring its spectral area, that is directly proportional to the mole fraction itself. The estimate of the ^{14}C content in each sample is obtained with a relative measurement, by comparing the spectral areas of the unknown sample and a standard reference material (SRM)(^{2}). Each acquisition (6 min duration) is performed by scanning (650 MHz span) step-wise (10 MHz step) the frequency across the target transition back-and-forth. For each frequency point, 5000 SCAR signals are acquired and averaged. The values of the gas-induced cavity decay rate belonging to the single sweeps are averaged together, thus yielding the function $\gamma_g(\nu)$. For each sample, 28 spectra of γ_g across the P(20) line are recorded and data are fitted to a two-line manifold Voigt profile, that was chosen considering the target line of $^{14}CO_2$ and an interfering line of N_2O at 2209.0854 cm^{-1}, though always strongly suppressed during sample preparation. Figure 2 shows the average of 28 measurements of the KB sample. The measured spectrum was fit to a 2-Voigt function, taking into account both the $^{14}CO_2$ peak (orange shaded area) and the small interfering N_2O peak (yellow shaded area). Fit residuals are shown at the bottom. The grey shaded area represents the fit result for the SRM and is used to calculate the ^{14}C content in all samples.

(^{2}) Oxalic acid dihydrate ($C_2H_2O_4 \cdot 2H_2O$) provided by the National Institute of Standards and Technology (SRM 4990C) with a carbon mass fraction of ∼ 19% and a ^{14}C mole fraction of 1.3407 $F^{14}C$

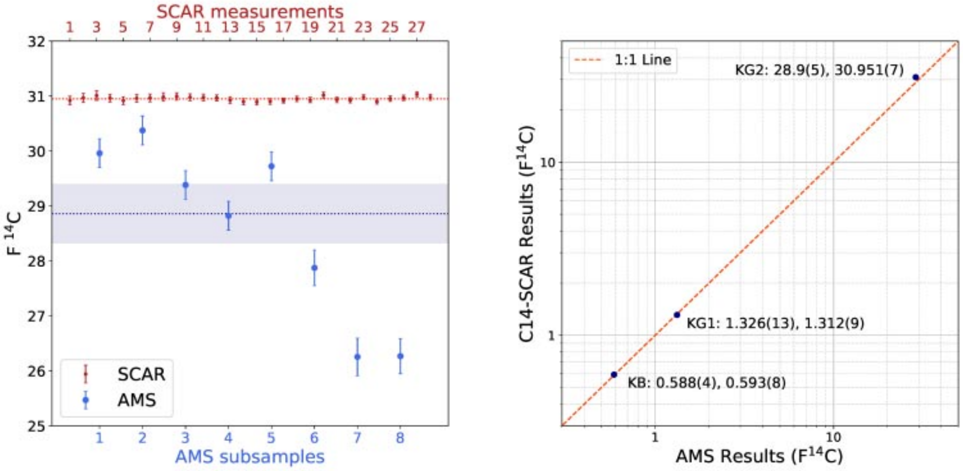

Fig. 3. – Left panel: measurements of the KG2 sample; SCAR results (red points) refer to the repeated measurements of the same gas sample produced by a single combustion, while AMS points (blue points) refer to gas samples produced by the combustion of different subsamples; the dotted lines and the shaded areas represent the weighted means and their uncertainties for the two techniques, respectively. Right panel: comparison between the weighted means obtained with the two techniques for the three samples.

3. – Results and discussion

The AMS results from all the sub-samples analyses were provided by the University of Cologne team. While no dilution was required for the SCAR analyses, for KG2 the addition of fossil graphite was needed, resulting in a dilution factor of 10.977. In fig. 3 left we report the measurement results for the KG2 sample obtained via AMS and SCAR. For each sample, 28 repeated measurements were performed with the SCAR method, while a single measurement on 10 different sub-samples was performed with AMS. One AMS measurement for KG1 and two for KG2 were excluded from the plot and from the statistical analysis, because affected by a systematic "memory" effect due to previously measured enriched samples.

As a consequence of the Poissonian statistics of the ion counting process, the AMS reported uncertainty is, as expected, about 1% for all measurements, while the SCAR uncertainty is about 0.03 $F^{14}C$ for all measurements, depending on the signal-to-noise ratio of the raw data and on the acquisition parameters [10]. Both for AMS and SCAR measurements, the weighted average and its uncertainty were calculated to obtain the final ^{14}C content value for each of the KB, KG1 and KG2 samples. The results are plotted in fig. 3 right. While for the KB and KG1 samples AMS and SCAR provide the same results, for the KG2 sample the two techniques are not providing statistically compatible results. Indeed, when comparing the AMS and SCAR datasets, a trend is evident in the AMS data plotted in fig. 3 left. We believe that possible inhomogeneity in the original KG2 sample can impact the results of this technique, since the AMS measurement is performed on different sub-samples. We also believe that the SCAR results for the KG2 sample are correct, while those provided by the AMS technique can be affected by a systematic error that was not possible to identify. Indeed, the two techniques provide consistent results for KB and KG1 samples and the linearity of the optical method was already demonstrated in the past [18].

4. – Conclusions

We have shown that, for ^{14}C detection in CO$_2$, laser spectroscopy achieves results similar to those obtained by AMS and, for highly enriched samples, is much better performing. Indeed, memory effects that can bias AMS results are not observed in SCAR analysis, that boasts a dynamic range for ^{14}C mole fractions that is 1-2 orders of magnitude wider than that of AMS, which is better suited for very low mole fraction values. Moreover, the small size and intrinsic portability has no match with even last generation, smaller AMS devices. This suggests three main areas of applications for SCAR analyzers. In Technology Parks, applications to radioactive waste of interest can be further studied, with different materials and ^{14}C levels, to refine the technique. This would require a dedicated laboratory, in which laser scientists can better focus the SCAR technique collaborating with people involved in radioactive waste treatment. A second possible application of SCAR mostly relies on its unmatched transportability. Indeed, nuclear sites of interest can be patrolled by SCAR devices looking for direct emissions of ^{14}CO$_2$ or for properly pre-treated materials. A third, more standard, application is with a fixed-position station for continuous measurement of ^{14}CO$_2$ from pre-treated and burnt samples.

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