



CHANCE Project

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Report on validation of transitions of rotation / vibration of HCl, specification and development of the equipment

DELIVERABLE (D5.1) Work Package 5 -Task 5.1

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ABSTRACT/CONCLUSION (subject to the same level of confidentiality as the rest of the document)

This work represents the D5.1 deliverable of the work package 5-task 5.1 of the Characterization of conditioned nuclear waste for its safe disposal in Europe (CHANCE) project.

The objectives of this study are to advance the use of CRDS as an innovative technique to characterize the outgassing of radioactive waste by developing a new instrumentation for ^{36}Cl measurement, as H^{36}Cl molecule, and to demonstrate an application of the technique to the monitoring of the radiocarbon outgassing.

In this deliverable, theoretical simulation of transitions of rotation / vibration on HCl, as well specification and development of the CRDS equipment are presented.

CRDS is a molecular laser absorption spectroscopy analysis technic. As H^{36}Cl has never been measured with such a technic, its rotation-vibration transitions were calculated using its isotopologs, H^{35}Cl and H^{37}Cl , spectroscopic characteristics available in HITRAN database. The calculation accuracy was validated and is considered sufficient for H^{36}Cl characterisation. H^{36}Cl rotation-vibration transition peak is positioned at **5737.15 cm^{-1}** . Considering presumed measurement conditions and technical characteristics of specific equipment, a theoretical detection limit was estimated between **0.2** and **15 ppb**, which depends on the relative position of H_2O and of H^{36}Cl wavelengths and on the water concentration in the sample. (D5.1)

Technical specifications for a CRDS equipment were defined and a call for tender was launched in 2018. The AP2E company was the only one proposing a CRDS equipment suitable for ^{36}Cl measurement.

The equipment was delivered with a delay of about three month, in June 2019. Measurement tests on a H^{36}Cl aqueous solution are the work of the deliverable D.2.

Experimental measurements using the developed CRDS equipment on graphite samples are expected (D5.3).

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1. INTRODUCTION AND OBJECTIVES

The CHANCE project [1] aims to address the specific issue of the characterization of conditioned radioactive waste. The characterization of fully or partly conditioned radioactive waste is a particular problem because unlike for raw waste, its characterization is more complex and needs specific non-destructive techniques and methodologies.

The first objective of the CHANCE project is to establish, at the European level, a comprehensive understanding of current conditioned radioactive waste characterization and quality control schemes across the variety of different national radioactive waste management programmes, based on inputs from end-users members such as Waste Management Organizations and storage operators.

The second objective of CHANCE is to further develop, test and validate techniques already identified that will improve the characterization of conditioned radioactive waste, namely those that cannot be easily dealt by using conventional methods. Specifically, the work on conditioned radioactive waste characterization technology will focus on:

- Calorimetry as an innovative non-destructive technique to reduce uncertainties on the inventory of radionuclides;
- Muon Tomography to address the specific issue of non-destructive control of the content of large volume nuclear waste;
- Cavity Ring-Down Spectroscopy (CRDS) as an innovative technique to characterize outgassing of radioactive waste.

The present report focuses on activities from Work Package 5. The objectives of this WP are to advance the use of CRDS as an innovative technique to characterize the outgassing of radioactive waste by developing a new instrumentation for ^{36}Cl measurement, as H^{36}Cl molecule, and to demonstrate an application of the technique to the monitoring of the radiocarbon outgassing.

This document constitutes the deliverable D5.1 of the task 5.1 about the theoretical simulation of transitions of rotation / vibration on HCl, specification and development of the CRDS equipment.

1.1 DESCRIPTION OF WORK PACKAGE 5

The development of the H^{36}Cl measurement with CRDS technique is based on knowledge of its application for non radioactive elements measurements and needs to be adapted and validated by simulation and experiments.

Task 5.1 of the work package 5 (WP 5) includes:

- theoretical validation of the rotation/vibration properties of the H^{36}Cl molecule by calculation of the frequencies and strength of the transitions (D5.1) ;
- specifications and development of an equipment dedicated to ^{36}Cl measurements (D5.1);
- experimental validation of the transitions with ^{36}Cl standards and an evaluation of the detection limit. (D5.2) Because only Na^{36}Cl liquid standards are available, this work requires first the chemical transformation of Na^{36}Cl into H^{36}Cl , before measurements with CRDS equipment.
- some experimental measurements using the developed CRDS equipment on graphite samples already available at CEA and CRDS performances comparison with liquid scintillation counting (D5.3).

1.2 REFERENCES

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1.3 GLOSSARY

CEA	French Alternative Energies and Atomic Energy Commission
DEN	Nuclear Energy Division
CAD	CADarache Center
DTN	Nuclear Technology Department
SMTA	Measurements and modeling of Transfers and Severe Accidents Section
LMCT	Laboratory for Mastering contamination and chemistry of Coolants and Tritium

2. ³⁶CL CHARACTERISTICS

Chlorine (atomic number $Z = 17$), a very electronegative and reactive halogen element, is commonly used in chemical and pharmaceutical industry processes. It is naturally present in oceans and seas as salt [2].

It has 14 isotopes from atomic numbers $A=32$ to 43 . Except ³⁵Cl and ³⁷Cl, all are radioactive. Only ³⁶Cl is to be considered as having a radioecological impact because the half-lives of other ones are too short (less than one hour). ³⁶Cl half-life is $3.02 \cdot 10^5$ years. It's principal decay mode is a β^- emission producing ³⁶Ar ($E_{\max} = 0.71$ MeV -98 %) and the remaining decay mode is an electron capture producing ³⁶S ($E_{\max} = 1.14$ MeV-2 %).

³⁶Cl is naturally produced in the atmosphere by cosmic rays and in the ground by activation. Its artificial presence is due to the nuclear bomb tests (1945-1962). It is also produced in nuclear reactors by stable chlorine (³⁵Cl) activation, hence it can be found in the nuclear reactor waste. It is outgassing as Cl₂ and HCl molecules from the waste packages [3].

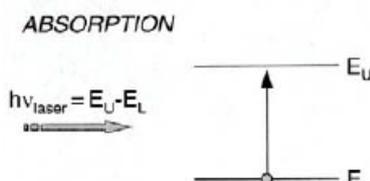
³⁶Cl is commonly measured by liquid scintillation technique after radiochemical separation from other beta-emitting radionuclides if present. This measurement requires the use of a liquid scintillation detector, after calibration of the equipment with a ³⁶Cl reference. Samples have to be conditioned in liquid form and mixed with a scintillation organic liquid adapted to ³⁶Cl measurement. Measurement time depends on the activity of the samples. A minimum of half an hour is usually needed if the sample's activity is sufficient.

3. CRDS PRINCIPLE AND ADAPTATION FOR H³⁶CL MEASUREMENTS

3.1 CRDS PRINCIPLE

Cavity Ring-Down Spectroscopy (CRDS) is one of the optical analysis technics which are based on atomic and molecular spectroscopy, involving electronic transitions (atoms and molecules) and rotation-vibration transitions (molecules) [3]. Vibration transitions are observed in the Narrow Infrared (NIR) and Mean InfraRed (MIR) domain and rotation transitions in FarInfraRed (FIR) scale.

The absorption spectroscopy principle lays on the absorption of light (photons) by atoms and molecules of the studied species. The photon energy corresponds to the transition energy between the stable (E_L) and the excited (E_U) level of the studied species. The light attenuation obeys the Beer-Lambert law. It depends on the studied medium, (chemical species concentration n), on the efficient cross section $\sigma(\nu)$ of the optical transition at a characteristic wavelength ν , and on the optical length, L , as:



$$I(\nu) = I_0(\nu) \exp[-n\sigma(\nu)L]$$

with $I_0(\nu)$, the initial light intensity and $I(\nu)$, the attenuated light intensity. CRDS analysis principle is valid in transparent media (classically gas or liquid).

CRDS is one of laser light absorption technics, which are not sensitive for homonuclear molecules as H₂ or Cl₂, because these molecules don't have a dipolar moment so only heteronuclear molecules as H₂O, HCl or CH₄ can be measured with CRDS. It is a very sensitive and selective technique for gas analysis [4].

Figure 1 presents a diagram of the general principle of a CRDS measurement device. The gas to be analysed is injected in an optical cavity, equipped with reflecting mirrors. The laser beam, accorded to an intense, characteristic of the element to measure, transition passes in the cavity and goes back and forth through the mirrors several times so as the light intensity decreases (the optical length L is increased by the reflections).

This intensity decrease yields an extinction time, the ringdown, τ_0 , characteristic of the cavity (free of absorbent medium), function of the optical length, L , and of the mirrors reflectivity, R . When absorbent species, with an absorption coefficient, $\alpha(\nu)$, are present in the cavity, the ringdown decreases according to the equation:

$$\tau(\nu) = \frac{L}{c[1 - R + \alpha(\nu)L]}$$

with c , light speed.

As the ringdown is a direct function of the absorption coefficient it is possible to determine the gas species concentration. No calibration is needed.

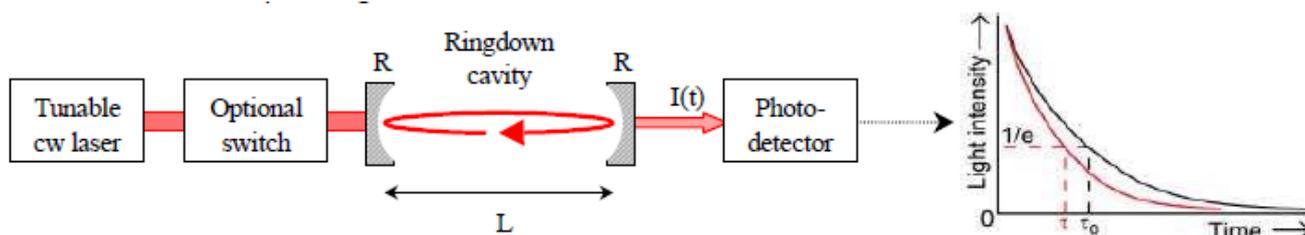


Figure 1 : CRDS principle diagram

3.2 CRDS ADAPTATION FOR H³⁶Cl MEASUREMENTS

CRDS technic is already used to measure different stable molecules as CO, CO₂, H₂S, CH₄, C₂H₄, or HCl and was particularly employed for climate and environmental topics [5]. Some studies were undertaken to show the interest for CRDS applications for radioactive molecule measures [4].

Several commercial CRDS systems for gas analysis are available. American companies as Picarro, Tiger Optics or Los Gatos Research and the French company AP2E manufacture such equipment.

The Laboratory of Physical Spectrometry of the University Joseph Fourier (UJF) in Grenoble developed a new fast, low-noise, mode-by-mode, cavity-enhanced absorption spectroscopy system [6]. It is called Optical Feedback Cavity Enhanced Absorption Spectroscopy (OF-CEAS). In such a system, after the laser emission, a part of the cavity light is injected again in the laser source, which results in an improvement of the quality of the laser light emitted and of the detection quality (reduction of the noise, improvement of the selectivity). A license was accorded to AP2E company to develop a commercial equipment of this system.

A part of CRDS study carried out by LRMO laboratory in CEA of Saclay was transferred to CEA-Cadarache for development of this technique for ³H outgassing measurements. It was assigned to LMCT laboratory in CEA of Cadarache, a laboratory carrying out studies involving different radionuclides, and particularly ³H and ³⁶Cl. Those radionuclides are usually measured in this laboratory with classical nuclear technics as liquid scintillation counting, after sample preparation (separation of radionuclides by radiochemical treatments). The CEA relies on the skills of the specialized society to analyze the CRDS measurements.

3.2.1 Theoretical study of HCl spectroscopic parameters

As noted in paragraph 3.1, CRDS measures are based on the knowledge of rotation-vibration transition energies of heteronuclear molecules. As ³⁶Cl outgases from nuclear graphite waste packages in the form of Cl₂ and HCl, only the HCl form could be detected by CRDS.

Isotopologues (chemically similar molecules with different isotopic compositions) of a chemical species, for example H₂O, D₂O (D = deuterium) and HTO (T = tritium), have different masses, because of their different isotopes. For that reason, rotation and vibration energy levels are modified, which involves a modification of the transition frequency (or wavenumber). The dipolar moment of the transition is not modified which means that the cross section is the same for the isotopologists. It is then possible, knowing spectroscopic parameters of a molecule, to determine by calculation the transition frequencies of its isotopologists. As a consequence, knowing rotation and vibration constants of H³⁵Cl and H³⁷Cl, H³⁶Cl transition constants can be calculated.

Molecular absorption characteristics of 49 molecules can be found in the HITRAN (**H**igh **R**esolution **T**ransmission) database [7] which is a compilation of spectroscopic parameters that are used to predict and simulate the transmission and emission of light in gaseous media (atmosphere, laboratory cells,). A paper [8] presents the last evolutions of this database up to 2016.

HCl isotopologues, H^{35}Cl and H^{37}Cl , rotation and vibration constants are available and a theoretical study, carried out by the LRMO laboratory in CEA of Saclay [4], showed that H^{35}Cl is easily detected in narrow infrared (14000-4000 cm^{-1}) domain with a good sensitivity and selectivity on the R3 transition of the 2-0-R branch harmonic, at 5739.26 cm^{-1} (1742 nm). Using this transition, it is also possible to detect the ^{37}Cl with the H^{37}Cl molecule at 5735.11 cm^{-1} (isotopic shift is -4.15 cm^{-1}). Calculated H^{35}Cl and H^{37}Cl rotation and vibration transitions of the 2-0 harmonic are compared with the HITRAN database data. It was considered that if the error between calculation and experimental results is lower than 0.1 cm^{-1} , the calculated results can be validated. This was obtained for the H^{35}Cl and H^{37}Cl more intense transitions, so the calculation results were validated for those two isotopologues. **Figure 2** presents an example of H^{35}Cl and H^{37}Cl CRDS measures in hydrogen chloride vapour and a comparison with calculation results with the expected accuracy. Blue line represents experimental points, the red one represents calculation results [4].

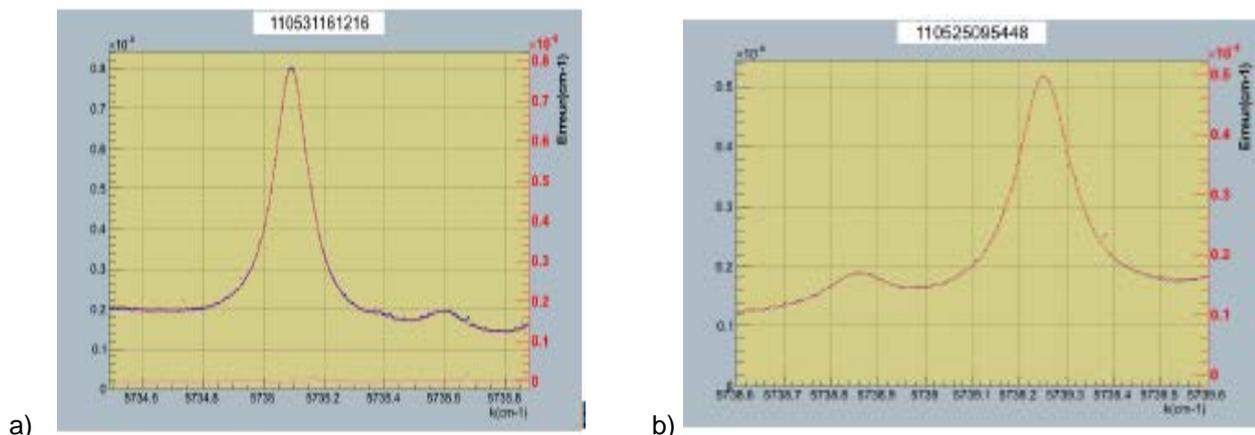


Figure 2 : CRDS HCl vapour measures: a) 15 ppm H^{37}Cl , b) 43 ppb H^{35}Cl . Blue experimental, red calculated [4]

Then, using the same accuracy, the same method was used for H^{36}Cl rotation-vibration transitions calculations. Isotopic shift is -2.11 cm^{-1} for H^{36}Cl , so the theoretical position of H^{36}Cl is 5737.15 cm^{-1} . Integrated intensities of the 2-0 harmonic rotation transitions of H^{35}Cl , H^{37}Cl and H^{36}Cl as a function of the wavenumber are plotted on the **Figure 3**.

Though no experimental results are available for H^{36}Cl to validate the calculation, it can be noted that H^{36}Cl transitions are positioned satisfactorily between the H^{35}Cl and H^{37}Cl ones, according to masses of the three chlorine isotopes. It was considered that calculation accuracy is good enough to characterise H^{36}Cl (identification, discrimination from interfering species and quantification). Detection limit, without taking any interferences, was estimated around several **ppb** (molar fraction), which is similar to the stable isotopes detection limit.

Detection limit depends not only on the spectroscopic characteristics of a molecule, as intensity of the transition or position of the line, but also on technical characteristics as mirrors reflectivity or sample composition. Calculations of the H^{36}Cl detection limit must be adjusted considering those characteristics. This part of work is advanced at LMCT in CEA Cadarache with support of AP2E company and presented in this deliverable (D5.1).

Those theoretical data have to be confirmed by measures with a specific CRDS device. This work will be presented in deliverable 5.2.

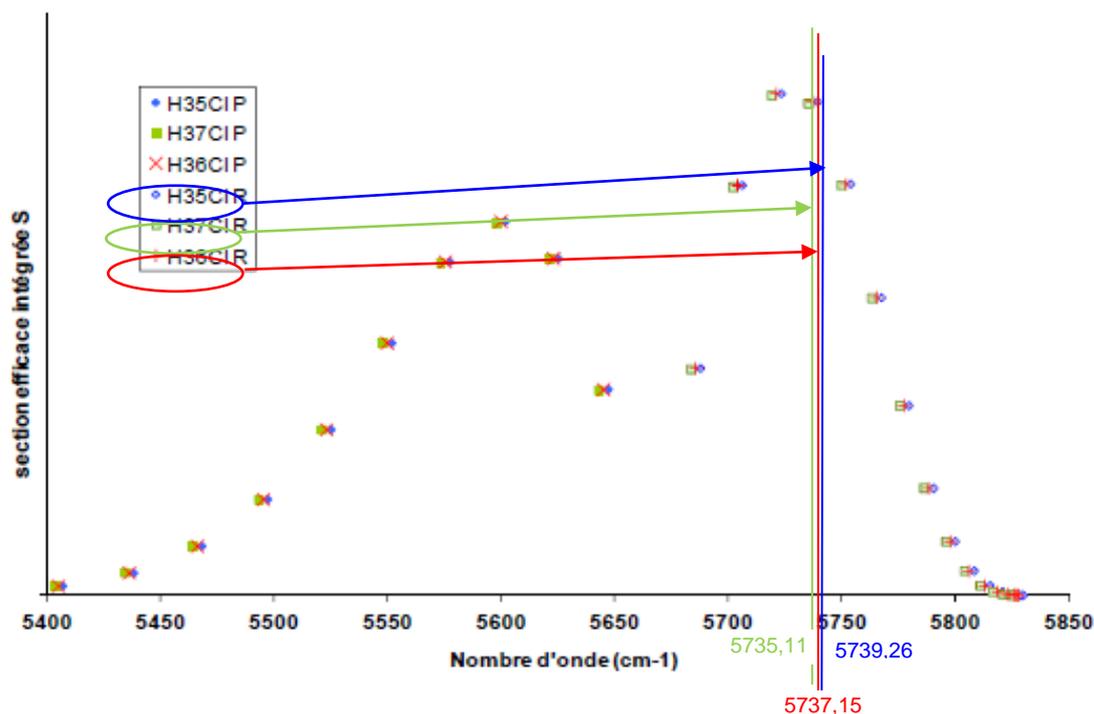


Figure 3 : Integrated intensities (or integrated cross sections) of the 2-0 harmonic rotation transitions (P and R branch) for $H^{35}Cl$, $H^{37}Cl$ and $H^{36}Cl$ (y axis) as a function of the wavenumber (x axis) [4]

3.2.2 Complementary calculations of the detection limit

As one of the objectives of the WP 5 is to evaluate the capacity of CRDS to detect and quantify $H^{36}Cl$ release from waste outgassing, it is important to evaluate its detection limit. This limit was evaluated theoretically by LRMO before the CHANCE project. To a complementary study of the detection limit of $H^{36}Cl$ using OFCEAS technology was then carried out by AP2E [9], a company specialised in CRDS devices for gas measures (H_2 , O_2 , HF , CH_4 , HCl ...) fabrication, using the UJF license (see § 3.2 and 3.2.3). It is based on previous knowledge on spectroscopic data of HCl isotopologues and on the AP2E OFCEAS analyser's characteristics (3.2.2.1). It also takes in account interferences due to water presence (3.2.2.2).

3.2.2.1 Theoretical detection limit of gaseous $H^{36}Cl$

$H^{36}Cl$ detection limit was evaluated by AP2E based on the Voigt model [7], [9]. First $H^{35}Cl$ detection limit was calculated with spectroscopic parameters of the molecule (HITRAN database) [7], considering theoretical measurement conditions and supposed device characteristics. The same calculations were made for $H^{36}Cl$, using theoretical spectroscopic parameters previously calculated. Parameters used and calculations are presented in the **Table 1**.

First, the spectral line of the molecule, which is broadened under external conditions, is simulated. It can be represented in the form of a distribution curve obtained using the Voigt profile, $\Delta\nu_{voigt}$, which is a convolution of Doppler profile, $\Delta\nu_{Doppler}$, and Lorentz profile, $\Delta\nu_L$. The Doppler profile, represented by a Gaussian, is described with the equation (1), the Lorentz profile with the equation (2) and Voigt profile with the equation (3) (**Table 1**).

Those profiles are used to estimate the absorption cross section of the molecule with the equation (4). Then it is necessary to know the molecular density in the cavity, which is dependent on temperature and pressure conditions (equation (5)). It is considered that during the measurements the gas fills 100 % of the cavity. The light absorbed quantity is dependent on molecular density and absorption cross section (6).

As $H^{36}Cl$ spectroscopic parameters are not available in HITRAN database, the environment-broadened half width of the spectral line, L_{env} , for this molecule is supposed equal to the $H^{35}Cl$ (at 5739.26 cm^{-1}) and $H^{37}Cl$ (at 5735.11 cm^{-1}) value. The $H^{36}Cl$ transition intensity is calculated as the average of $H^{35}Cl$ and $H^{37}Cl$ transition intensities ($8.242 \cdot 10^{-21}\text{ cm/molecule}$).

The detection limit is dependent on the light absorbed quantity and on the lowest amount of substance that can be detected with the OFCEAS AP2E device. **Considering conditions without interferences, $H^{35}Cl$ limit detection is about 0.7 ppb and $H^{36}Cl$ limit detection is about 1 ppb.**

	H ³⁵ Cl	H ³⁶ Cl
ϑ_0 (cm ⁻¹), absorption line wavenumber	5739.26 cm ⁻¹	5737.15 cm ⁻¹
k (J.K ⁻¹), Boltzmann constant	1.38x10 ⁻²³ J.K ⁻¹	1.38x10 ⁻²³ J.K ⁻¹
T (°K), measurement temperature	55 °C with the OFCEAS AP2E analyser	55 °C with the OFCEAS AP2E analyser
c (m.s ⁻¹), light velocity	2.998.10 ⁸ m.s ⁻¹	2.998.10 ⁸ m.s ⁻¹
M (kg), molecular mass	H ³⁵ Cl molar mass x 1.66.10 ⁻²⁷ kg	H ³⁶ Cl molar mass x 1.66.10 ⁻²⁷ kg
Doppler profile : $\Delta\vartheta_{Doppler}$ (cm ⁻¹) = $2\vartheta_0\sqrt{\frac{2kT\ln(2)}{Mc^2}}$ (1)	0.0124 cm ⁻¹	0.0122 cm ⁻¹
L_{env} (cm ⁻¹), environment – broadened half width of a spectral line at the half – maximum of the probability at reference temperature	0.05 cm ⁻¹	0.05 cm ⁻¹
N_t , temperature – dependence exponent for L_{env}	0.5 (without dimension)	0.5 (without dimension)
P (bar), measurement pressure	50 mbar with the OFCEAS AP2E analyser	50 mbar with the OFCEAS AP2E analyser
P_{ref} (bar), reference pressure	1 bar	1 bar
Lorentz profile : $\Delta\vartheta_L$ (cm ⁻¹) = $2.L_{env}.f(P,T) = 2.L_{env}\left(\frac{P}{P_{ref}}\right)\left(\frac{296}{T}\right)^{N_t}$ (2)	4.749.10 ⁻³ cm ⁻¹	4.749.10 ⁻³ cm ⁻¹
Voigt profile : $\Delta\vartheta_{Voigt}$ (cm ⁻¹) = $0.5346\Delta\vartheta_L + \sqrt{0.2166\Delta\vartheta_L^2 + \Delta\vartheta_{Doppler}^2}$ (3)	0.0151 cm ⁻¹	0.0149 cm ⁻¹
I (cm.molecule ⁻¹), transition intensity	1.25x10 ⁻²⁰ cm.molecule ⁻¹	8.242.10 ⁻²¹ cm.molecule ⁻¹
Absorption cross – section = σ (cm ² /molecule) = $\frac{2 \times I}{\pi \Delta\vartheta_{Voigt}}$ (4)	5.27.10 ⁻¹⁹ cm ² /molecule	3.521.10 ⁻¹⁹ cm ² /molecule
N_A , Avogadro number	6,02.10 ²³ molecule.mol ⁻¹	6,02.10 ²³ molecule.mol ⁻¹
V_m , molar volume	22,4 L.mol ⁻¹	22,4 L.mol ⁻¹
Molecular density, d (molecule.cm ⁻³) = $\frac{N_A}{V_M} \frac{P}{P_{atm}} \frac{T_0}{T}$ (5)	1.08.10 ¹⁸ molecule.cm ⁻³	1.08.10 ¹⁸ molecule.cm ⁻³
Light absorbed quantity (cm ⁻¹) = $d \times \sigma$ (6)	0.569 cm ⁻¹	0.380 cm ⁻¹
Minimum amount of substance detected OFCEAS AP2E advice	4.10 ⁻¹⁰ cm ⁻¹	4.10 ⁻¹⁰ cm ⁻¹
Detection limit(ppb) = $\frac{\text{Minimum amount of substance detected}}{\text{Light absorbed quantity}} 10^9$ (7)	0.703 ppb	1.053 ppb

Table 1: Spectroscopic and measurement parameters used for limit detection calculations

3.2.2.2 Evaluation of water influence on the detection limit

A calibration will be necessary for CRDS device development. As H^{36}Cl gas reference is not commercially available, this calibration will be operated with another form of this molecule. ^{36}Cl reference is a NaCl solution which should be transformed into HCl (this work is planned for the D.5.2 of CHANCE project) to be measured with the CRDS device. Reference samples which will be measured in lab tests will be aqueous solutions. It was, then, necessary to take into account water presence for the detection limit theoretical evaluation.

Water presence will modify measurement conditions. AP2E evaluated pressure with 100 % of water in the cavity to 25 mbar instead of 50 mbar for a gaseous sample. In those conditions, Voigt profile and molecular density will be modified and the new calculated H^{36}Cl detection limit will be about **2 ppb** but other influences more important than the simple pressure modification have to be considered. Indeed, it is difficult to evaluate the interference of water line on the H^{36}Cl line. A simulation of water and H^{36}Cl spectra was made by AP2E.

The H^{36}Cl spectrum was simulated with HITRAN's data for H^{35}Cl and the wavenumber shift of H^{36}Cl ray that was identified as 5737.15 cm^{-1} (see § 3.2.1). Water spectrum is represented on the blue curve (**Figure 4**). H^{36}Cl theoretical ray position is represented on the red curve. The red straight line represents the error of the H^{36}Cl ray with an accuracy of $\pm 0.1 \text{ cm}^{-1}$. If the real (experimentally validated) position of H^{36}Cl is lower than the one predicted, an interference with water ray will be observed and measures are expected to be more difficult. On the contrary, if the line position is situated at higher wave number, the identification of H^{36}Cl will be easier. For this reason, the ultimate limit of detection for a sample containing water can only be determined experimentally.

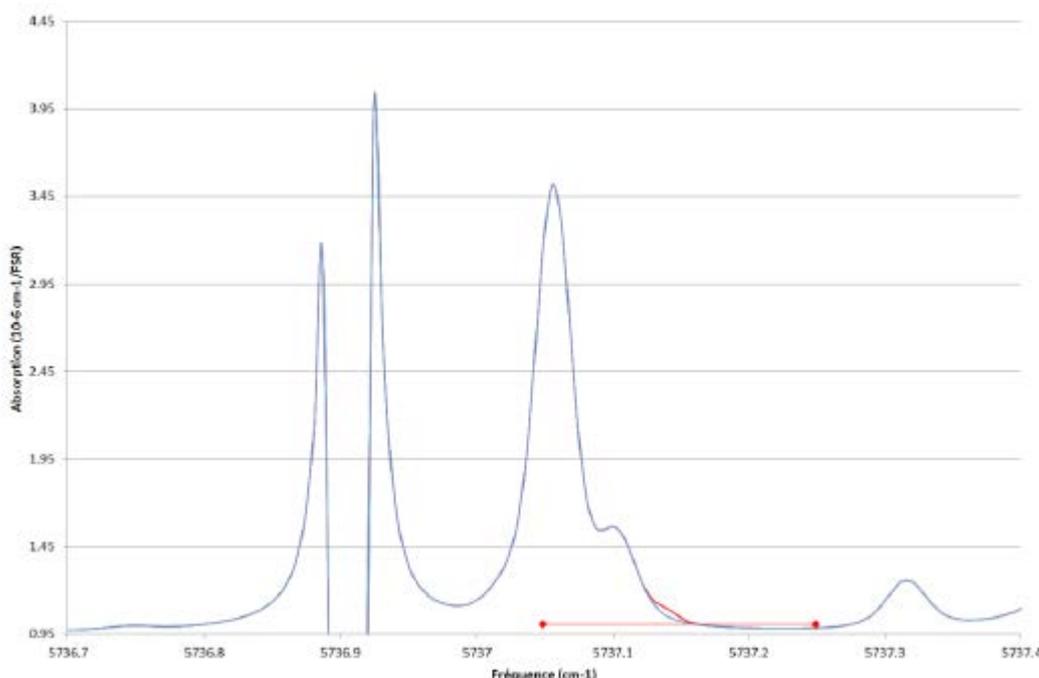


Figure 4 : OFCEAS simulated spectra of H^{36}Cl solution at 25 mbar with 5000 ppb of H^{36}Cl (red curve) and 100 % H_2O (blue curve) - Absorption as a function of wavenumber [9]

3.2.3 CRDS device development for ^{36}Cl measurement

Technical specifications for a CRDS equipment dedicated to ^{36}Cl measurements, with the objective to evaluate the detection limit in lab conditions, were defined and a call for tenders was launched in 2018. The AP2E company, specialized in CRDS gas analyzers manufacturing, was the only one proposing a CRDS equipment suitable for H^{36}Cl measurement.

The equipment proposed by AP2E in the technical offer, named PROCEAS, operates with the OFCEAS (Optical-Feedback Cavity Enhanced Absorption Spectroscopy) technology [10]. As the concentration of H^{36}Cl will be very low comparatively to other species (specifications for a detection limit of about 20 ppb) and particularly stable species as water, high reflectivity mirrors are used in such analyzers. Thanks to these mirrors, the quality of the optical path is

largely increased which makes possible to reduce detection limit and measurement time. The laser emission range is adapted to the theoretical H^{36}Cl absorption peak, between **5741.1 and 5735.6 cm^{-1}** .

This equipment has to be adapted to the specificity of study of the detection limit assessment (in lab case). In particular, the physico-chemical form of the sample has to be different from the standard ones measured by CRDS devices. PROCEAS analyzers usually operate by pumping ambient gas in the cavity for dynamic measures; the sampling system is situated on the side of the cell. In our study, liquid samples of a ^{36}Cl standard source will be used for calibration of the equipment and the measures will be performed in static mode. As the consequence, the injection system has been placed above the cavity and the injection of the aqueous sample will be operated with a syringe, through a septum (green disk on b) figure 5). About 0.5 to 3 μL of solution can be injected in the cavity and the measure is made in static mode. An example of a similar PROCEAS analyzer, prototype for HTO molecules (liquid form) measurement, is presented on **Figure 5**.

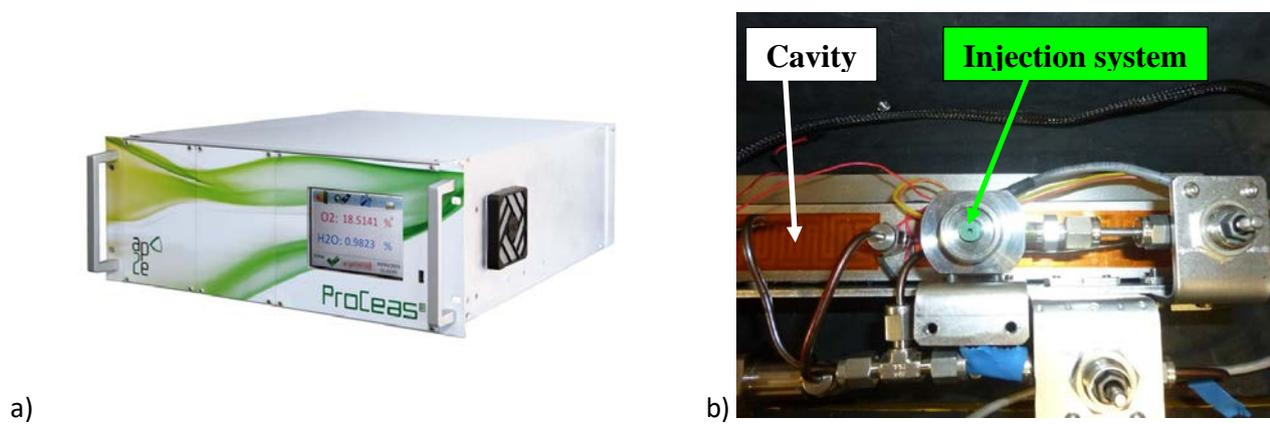


Figure 5 : PROCEAS analyser: general view a), upside view of the cavity b)

The delivery of the equipment and tests were foreseen between 4 and 5 months after the order (around end of March 2019) but an extension of delivery, due to component supply delay, was announced by AP2E. The equipment was delivered in June 2019. Several tests were led in the second part of 2019. The results will be presented in the D.5.2 deliverable.

4. CONCLUSION

The objectives of this study are to develop the use of Cavity Ring-Down Spectroscopy (CRDS), an optical analysis technique based on molecular spectroscopy, using LASER, as an innovative technique to characterize outgassing of radioactive waste and particularly ^{36}Cl as H^{36}Cl molecule.

As H^{36}Cl was never measured with such a technique, its spectroscopic characteristics are unknown. Using its isotopologues H^{35}Cl and H^{37}Cl spectroscopic characteristics, available in literature and especially in the HITRAN database, it was possible to calculate the H^{36}Cl rotation-vibration transitions (D5.1) with a good accuracy. H^{36}Cl transitions are positioned between the H^{35}Cl (**5739.26 cm^{-1}**) and H^{37}Cl (**5735.11 cm^{-1}**) ones, so the theoretical peak of H^{36}Cl is situated at **5737.15 cm^{-1}** .

It is considered that identification, discrimination from interfering molecules and quantification of H^{36}Cl molecule is possible. Considering conditions without interferences, H^{35}Cl limit detection is about 0.7 ppb and H^{36}Cl limit detection is about 1 ppb. A potential interference with water molecule was identified by the AP2E company which provided the prototype for H^{36}Cl measures, a PROCEAS analyser.

The equipment was delivered with a delay in June 2019. Measurement tests on a H^{36}Cl aqueous solution are the work of the deliverable D.5.2.