



IMPROVEMENT OF WASTE RELEASE CONTROL IN FRENCH NPP

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1. PRINCIPLES OF THE NEW LICENCE FOR WASTE RELEASES AND WATER SUPPLY

1.1. Environmental concerns of population

Problems of assessment and reduction of NPP impacts have been more and more important for last years. Though the 58 EDF nuclear reactors largely participate to the environmental protection (no greenhouse gas, no acidic pollutant, no dusts ..), evolving concerns of population lead to the evolution of the French regulation on the NPP releases. Moreover, EDF NPP operators have launched a voluntarist process to reduce their releases since the beginning and before the evolution of the regulation. EDF priorities in terms of environment care lead henceforth to implement a global optimisation of the impact for a better control of releases. In this view, EDF have decided to create a national laboratory in its nuclear industry branch : LAMEN (Analysis and Measurements Laboratory in Nuclear Environment). It will be in charge of various fields of interests :

- Gaseous and liquid wastes,
- Environmental controls,
- Post-accident measurements,
- Primary coolant radiochemistry.

1.2. Integrated licence for waste releases and water supply

Commercial operation of a nuclear power unit requires several licences. Until 1995, one licence was required for the water supply and another one for liquid and gaseous radioactive waste releases. In adequacy with the French law about water (1992) and with the ministerial decree (1995) and in case the renewal of the water supply licence is required, a French NPP needs to negotiate with the French administration a new licence, which covers water supply and waste releases ^(1,2).

The purpose of this ministerial order, signed by the ministers in charge of industry, health and environment, is to specify the limits for water supply and wastes releases (gaseous and liquid) and the frequency of all the specified controls. The main evolutions are a new distinction between radioactive wastes (there are specific limits for some radionuclides such as iodine, carbon 14 or rare gas), lower limits for activities, many more chemicals to control with lower maximum concentrations.

1.3. Limits for radioactive releases

Parameters (GBq)		PWR 900	PWR 900	PWR 1300	PWR 1300	PWR 1450
Old	New	Old	New	Old	New	
Tritium	Tritium	55 000	45 000	80 000	60 000	80 000
Radioelements Except ⁴⁰ K and radium	Iodines	750	0,3	1 100	0,1	222
	Other radioelements		30		25	
¹⁴ C	¹⁴ C	-	300	-	400	-

Table 1 : Limits of activity for liquid wastes for old and new licences (in GBq/year for 2 units).

Parameters (GBq)		PWR 900	PWR 900	PWR 1300	PWR 1300	PWR 1450
Old	New	Old	New	Old	New	
Gas	Tritium	1 150 000	4 000	1 650 000	5 000	330 000
	Rare gas		36 000		45 000	
	¹⁴ C	-	1 100	-	1 400	
Halogens and Aerosols	Iodines	37,5	0,8	55	0,8	11
	Other radioelements		0,8		0,8	

Table 2 : Limits of activity for gaseous wastes for old and new licences (in GBq/year for 2 units).

1.4. Limits for chemical releases

Chemicals	Concentrations in tanks (mg.kg ⁻¹)		Flux per 2 hours (kg)		Flux per day (kg)		Flux per year (kg)	
	Golfech (old)	St-Alban (new)	Golfech (old)	St-Alban (new)	Golfech (old)	St-Alban (new)	Golfech (old)	St-Alban (new)
Boric acid	-	14 300	5 000	300	8 500	3 000	-	23 000
Lithium Hydroxide	-	10	4	3	7	7	-	14
Morpholine	-	8	20	10	100	15	-	1 600
Hydrazine	-	0.1	250	7.2	500	9	-	150
Ammonia	-	1	-	80	-	100	-	1 100
Phosphate	-	200	-	120	-	150	-	4 000
Surfactant	-	-	-	160	-	200	-	3 000
COD	-	200	-	120	-	150	-	-
Suspended solids	-	35	-	42	-	120	-	-
Metals	-	5	-	2.5	-	5	-	270

Table 3 : Example of maximum values of the chemical wastes from the nuclear island and the conventional island for old and new licenses.

Chemicals	Control points		Frequency	
	Golfech (old)	St-Alban (new)	Golfech (old)	St-Alban (new)
Surfactant	Radioactive and conventional liquid waste	Radioactive liquid waste	1 per month on aliquot	Each release
Boric acid				Radioactive and conventional liquid waste
Lithium Hydroxide		Radioactive and conventional liquid waste		
Morpholine				1 per month on aliquot
Hydrazine			Each release	
Ammonia				1 per month on aliquot
Phosphate		Each release		
Chemical Oxygen Demand			1 per month on aliquot	
Suspended solids	Each release			
Metals		1 per month on aliquot		

Table 4 : Example of control points and frequencies for chemical analyses for old and new licences.

1.5. Constraints for chemical follow-up

The chemical release surveillance has been greatly evolving for some years. The previous licences legislated on taking into account a global view of the chemical release impact. Limits in flux and in concentration of soluble matters were settled without any chemical species distinction. Only one exception concerning chlorine was pointed out. In fact, there was a possibility to treat the cooling waters with sodium hypochlorite in order to fight the fouling of circuits.

The new licence notably involves all the products used in the process. They therefore foresee a surveillance concerning thirty different parameters. Limits are settled for each parameter in terms of 2 hours fluxes and 24 hours fluxes as well as for maximal allowed concentrations in the release channel and the outer surrounding. Added to that, there are controls in tanks before release which enables to respect these limits. The necessary

time to define the release conditions of the tanks (up to 10 parameters to control) is now an important criterion for operation. The operator must therefore choose the fastest methods in order to optimise his generation capacity.

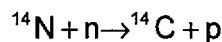
For example, eutrophication of the river Loire is a great concern during the summer period and so the regulation has pointed out phosphorus which is a main parameter for this phenomenon. The authorised limit is very low and thus leads to use an effective method with a very low detection limit. In addition, this method must rapidly be implemented for operation concern.

2. PARTICULAR CASE OF CARBON 14

Carbon 14 is a radionuclide of long half-time (5730 years). Carbon 14 decays in nitrogen 14 with β^- emission with a maximum energy of 156 keV. There is no significant γ radiation associated with this nuclear disintegration. This is the reason why carbon 14 is commonly measured by liquid scintillation counting or proportional counting.

2.1. Natural origin

Carbon 14 is produced in nature by (n,p) reaction on nitrogen in the upper atmosphere:



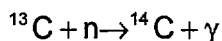
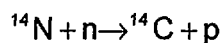
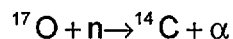
Today, the annual production rate is about 1.0 to $1.4 \cdot 10^{15}$ Bq ⁽⁴⁾ and the total reserve on earth is estimated to $1.11 \cdot 10^{19}$ Bq. This activity is in equilibrium : 90% is in the deep oceans, 1% in the atmosphere and 9% in the surface waters, sediments and biosphere. Two phenomena have lately modified this equilibrium and the specific activity of carbon 14 present in the atmosphere :

- The release of carbon dioxide linked to the use of fossil fuel without carbon 14 (this release has a dilution effect). This is known as the Suess effect.
- The human nuclear activities (mainly the atmospheric nuclear bomb tests).

2.2. Artificial origin

The main part of artificial carbon 14 comes from the atmospheric nuclear bomb tests. The estimate of the generated activity is about 220 to $355 \cdot 10^{15}$ Bq. This implicated the doubling of the specific activity of carbon 14 in air which was rapidly reduced by the Suess effect. The specific activity of carbon 14 in air was equal to 39 mBq/m³ in 1950, reached 67 mBq/m³ in 1965 and is now about 42 mBq/m³.

Carbon 14 is known to be also produced in a nuclear reactor by various reactions in the fuel, moderator and core construction materials. The production mechanisms include neutron-induced reactions and ternary fission :



The major part of carbon 14 release around a PWR comes from the oxygen 17 activation in the water coolant. The nitrogen 14 part depends on nitrogen concentration in water coolant and the contribution of carbon 13 is negligible. The gaseous and liquid releases can be related to the power generation : 220 GBq/GWe.year for the gaseous release and 15 GBq/GWe.year for the liquid releases. The gaseous release is composed of organic compounds (80% in methane form and other organic compounds) and carbon dioxide (20%).

The environmental impact of carbon 14 release is of great importance since its contribution to the collective effective dose is far higher than the contribution coming from the other radioactive contaminants. The main causes are the long half-time of this isotope, the biological importance of carbon but also the recent decreases of the releases of other radionuclides. These facts explain the evolution of the regulation concerning this radioactive isotope. Indeed, the new regulation summarized in chapter 1, gives specific limits for carbon 14 gaseous and liquid releases. Now, carbon 14 is a radioactive isotope under investigation for Saint-Laurent, Paluel, Flamanville, Belleville and Saint-Alban PWRs.

GDL (Corporate Laboratories of EDF Industry Branch) is in charge of developing the analytical techniques for carbon 14 measurements in liquid and gas wastes and also in the environment.

2.3. Measurement of carbon 14

2.3.1. Measurement in gaseous waste

Gaseous sampling is carried out with an automatic sampling machine (see figure 1) implemented at the NPP stack. A sample of the gaseous waste is first pumped, oxidised in a catalytic oven and then filtered on 300 grams of molecular sieves. Molecular sieves (zeolite structure) fully trap carbon dioxide and water present in the gaseous waste.

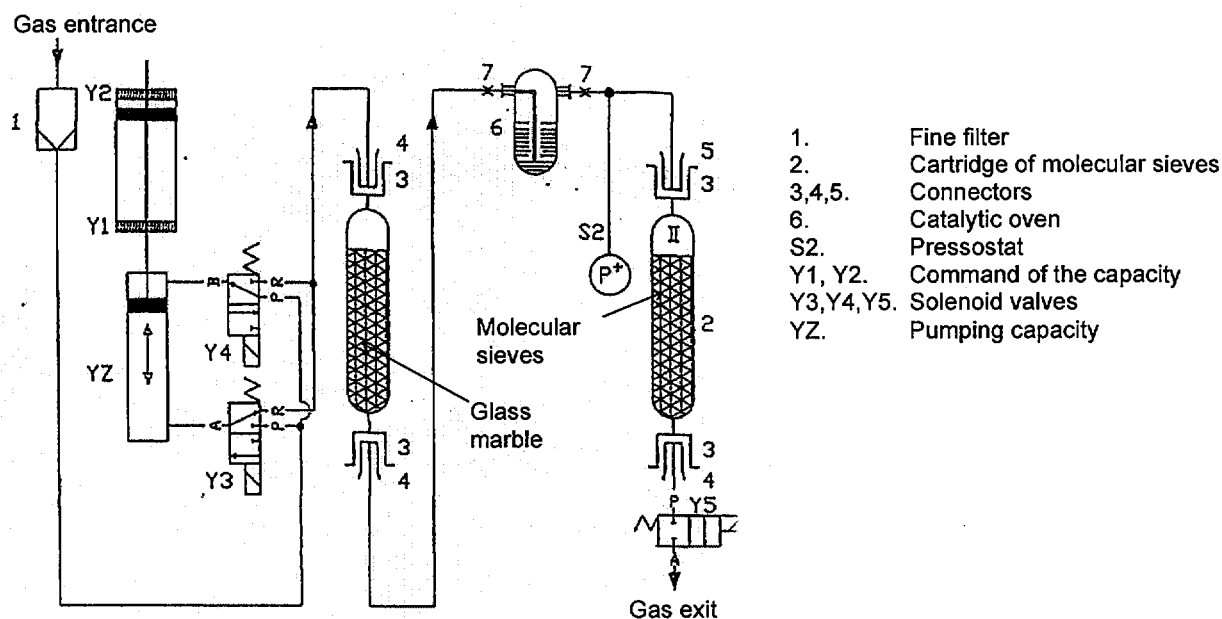


Figure 1 : Scheme of the sampling machine

At high temperature (400°C), molecular sieves release the carbon dioxide and the water previously trapped. The gas coming from desorption is driven to a column filled with sodium hydroxide. Carbon dioxide reacts with sodium hydroxide. Addition of barium chloride in sodium hydroxide precipitates barium carbonate. The precipitate is dried and grinded. A portion of the precipitate is measured by liquid scintillation counting. This method was developed by BfS⁽⁶⁾ (Bundesamt für Strahlenschutz). The minimum detectable activity obtained in EDF Chinon laboratory is about 200 mBq/m³.

2.3.2. Measurement in liquid waste

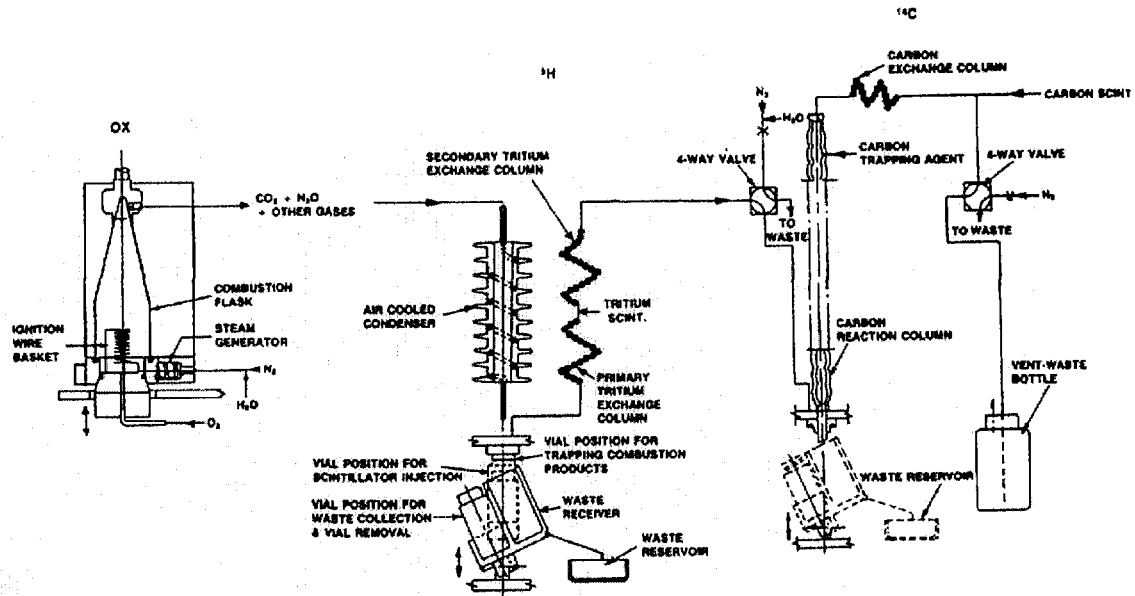


Figure 2 : Scheme of the "oxidiser" system

Concerning liquid wastes, an oxidation of a liquid sample is performed by an "oxidiser" (see figure 2). Carbon dioxide created is trapped in a reaction column filled with a specific liquid reagent. At the end of the combustion, the reaction column is rinsed by a scintillation cocktail. The rinsing effluent containing carbon 14 is directed into a vial. This vial is counted by liquid scintillation counting. The minimum detectable activity obtained in EDF Chinon laboratory is about 50 Bq/L.

2.3.3. Environmental control

As for the environmental measurement, two methods are currently used.

The first one uses two pair of columns filled with sodium hydroxide and separated by a catalytic oven. Measurement is performed on a portion of barium carbonate precipitate (just like for the carbon 14 measurement in gaseous waste). The major problem is the limitation in time of the sampling. Indeed, the sampling machine cannot be used over 15 days.

The second method which solves this drawback is to burn a dried vegetal sample taken from the surrounding of the NPP. The combustion is implemented in an "oxidiser" just like the carbon 14 measurement in liquid waste.

The first method has a minimum detectable activity of 200 mBq/m³. The second one is about 60 mBq per gram of dried vegetable (this is under the mass activity of natural carbon 14). Thus, the second method is easier to use and more sensitive than the first one.

2.3.4. Dosimetry

Since the origin of its nuclear plants, reduction of release impacts has been a constant EDF will. : the implemented actions permitted a decrease by a factor 100 over the last 10 years. At the starting point, tritium and carbon 14 impacts were negligible compared to the other contaminants. As it is technologically impossible to lower this two radionuclides in releases, our efforts have been focused on the other radionuclides part. Currently, the contribution of carbon 14 to the collective effective dose for the population living in the neighbourhood of a NPP is now preponderant.

The release impacts of NPP involves an increase of carbon 14 specific activity of 6 Bq per kg of carbon. This number can be compared to the specific activity of natural carbon 14 which is equal to 260 Bq per kg of carbon (the artificial contribution is practically undetectable). The collective effective dose due to a NPP for the population living around a NPP is lower than 1 µSv/year which can be compared to the mean dose due to natural radioactivity in France (2400 µSv/year).

3. ANALYTICAL METHOD LINKED TO THE NEW REGULATION

The evolution of the French regulation explained in chapter 1 leads to complete the laboratory analysis infrastructure with new reliable, simple and fast analytical techniques. Among these complementary techniques, UV spectrometry and capillary electrophoresis are studied by EDF.

Almost all the existing compounds absorb in the near UV region (between 200 and 350 nm) in aqueous solution. Thus, the UV optical properties of specific compounds can be selected to develop methods using the correlation between the concentration of one compound and its UV response. The methods developed by EdF, in collaboration with a French university (Ecole des Mines d'Alès), are based on multiwavelength procedures using the deconvolution principle, which enable to take into account the interferences from others component in the analytical treatment ⁽³⁾.

In practice, the shape of the UV spectrum can be considered as a linear combination of better-defined spectra (reference spectra REF1, ..., REFP) related to characteristic compounds of the water :

$$S_w = \sum_{i=1}^p a_i \cdot \text{REF}_i \pm r$$

Where a_i and r are respectively the coefficient of the i^{th} reference spectrum and the admitted error.

The general procedure is described in Figure 3. The acquisition of spectra is carried out between 205 and 330 nm with a PC controlled UV spectrophotometer.

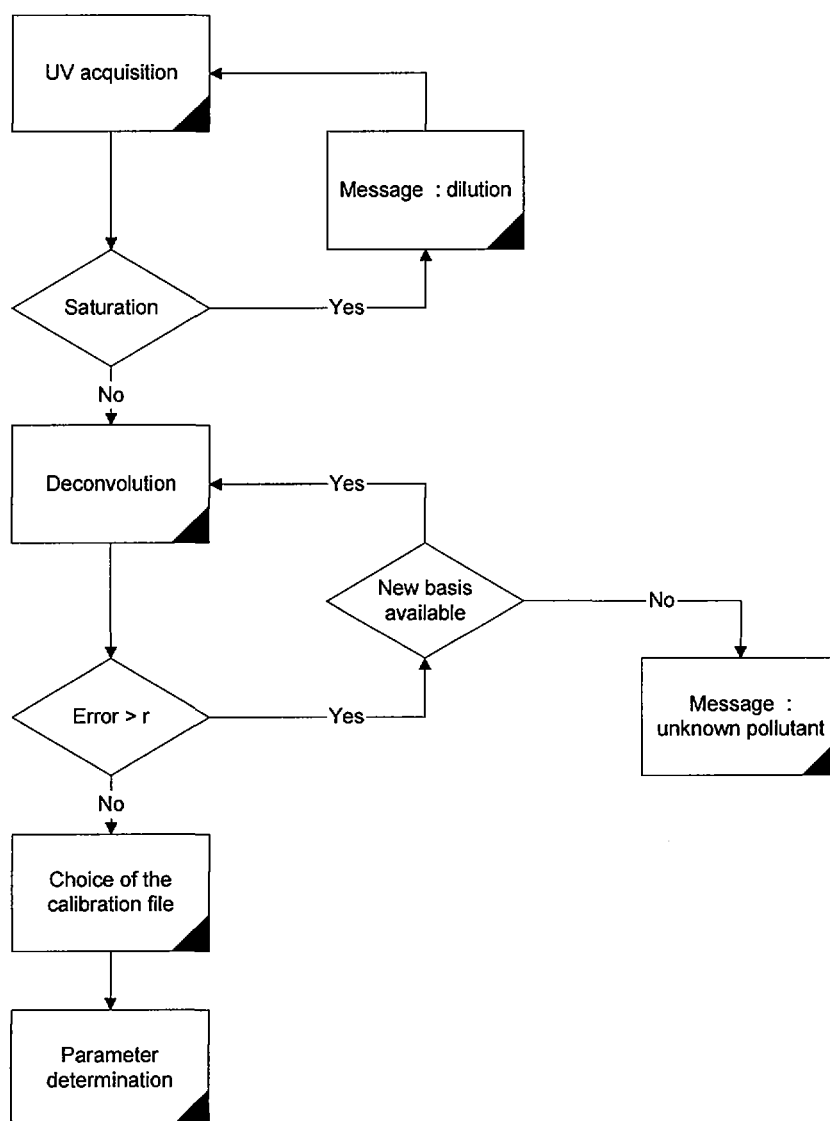


Figure 3 : Procedure for parameter determination after UV spectrum acquisition. The reliability of the method strongly depends on the choice of the reference spectra. In order to minimize the analytical bias, a basis with five

reference spectra corresponding to the different phases of absorbent matter and to specific compounds has been chosen (Figure 4) :

- REF1 : suspended matter
- REF2 : colloidal matter
- REF3 : dissolved absorbent matter
- REF4 : nitrate
- REF5 : surfactant

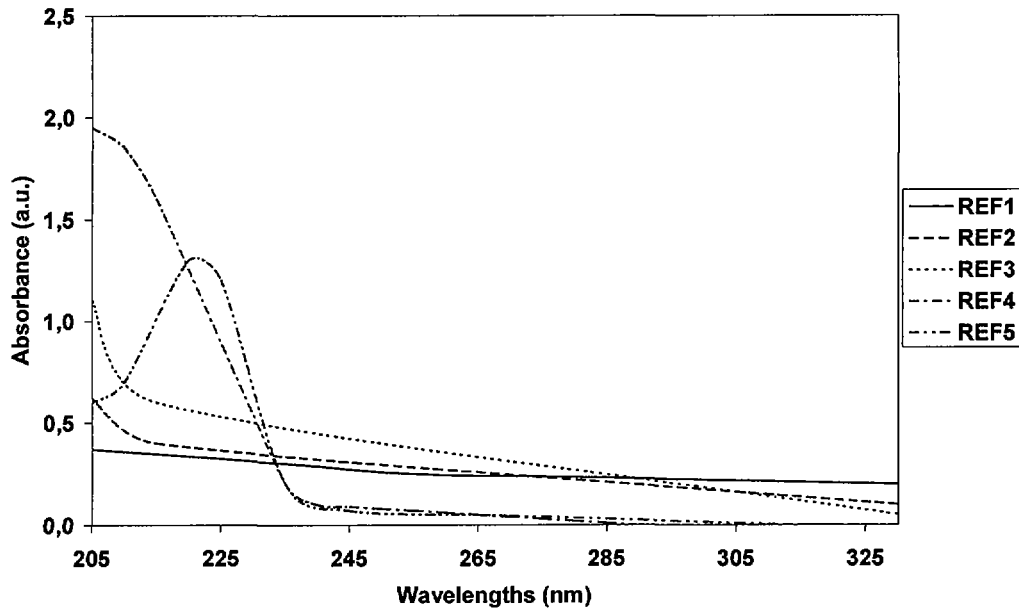


Figure 4 : Reference spectra

Once this basis of reference spectra has been selected, a sample can be analysed. After deconvolution, the sample spectrum is converted into a linear combination. The calculated coefficients of the reference spectra, leading to the restitution of the real spectrum, allow to obtain the composition of the sample. For instance, Figure 5 shows the deconvolution of a sample spectrum, characterized by a large contribution of reference spectrum REF4 and a negligible or very low participation of spectrum REF 5 in the restitution.

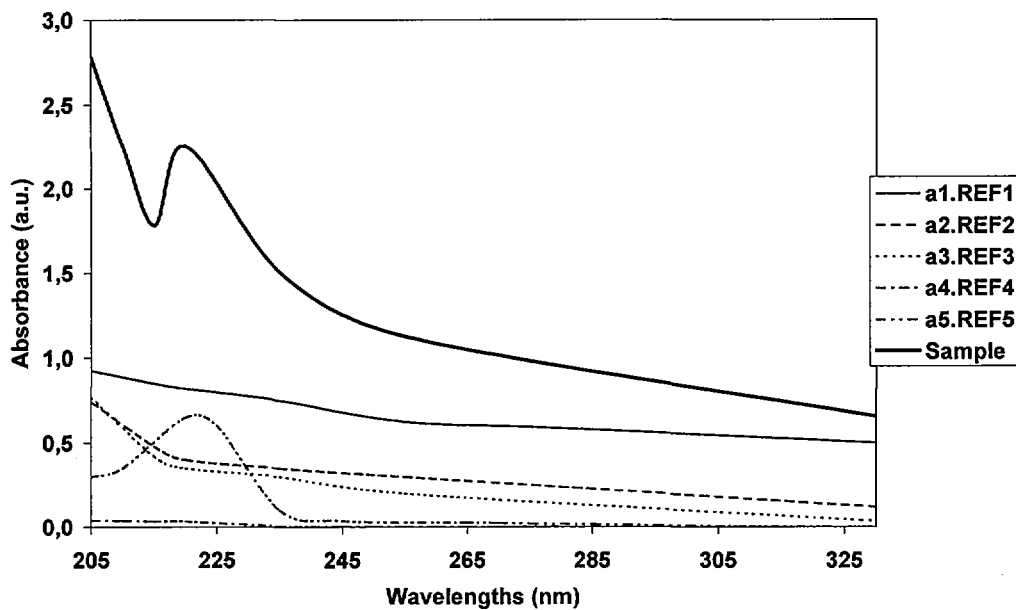


Figure 5 : Deconvolution of sample spectrum with the five reference spectra

Depending on the component to be determined, the sample will firstly be treated by complexation or photo-oxidation. Figure 6 shows how to proceed.

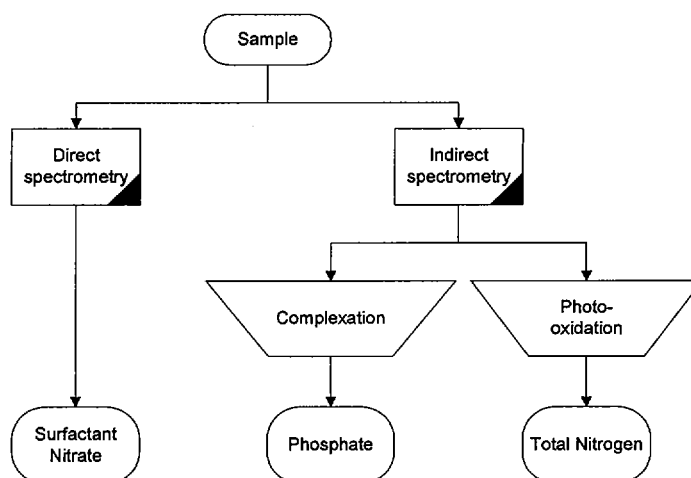


Figure 6 : Sample treatment

The UV spectrometry technique has been tested for 3 months on real samples taken from the conventional island liquid waste discharge systems of Paluel and Civaux NPP. As shown on figure 7, which compares the results of the analysis obtained by standard methods (NTK + NO_3^- + NO_2^-), the UV spectrometry appears accurate in the range 0-70 mg.kg^{-1} .

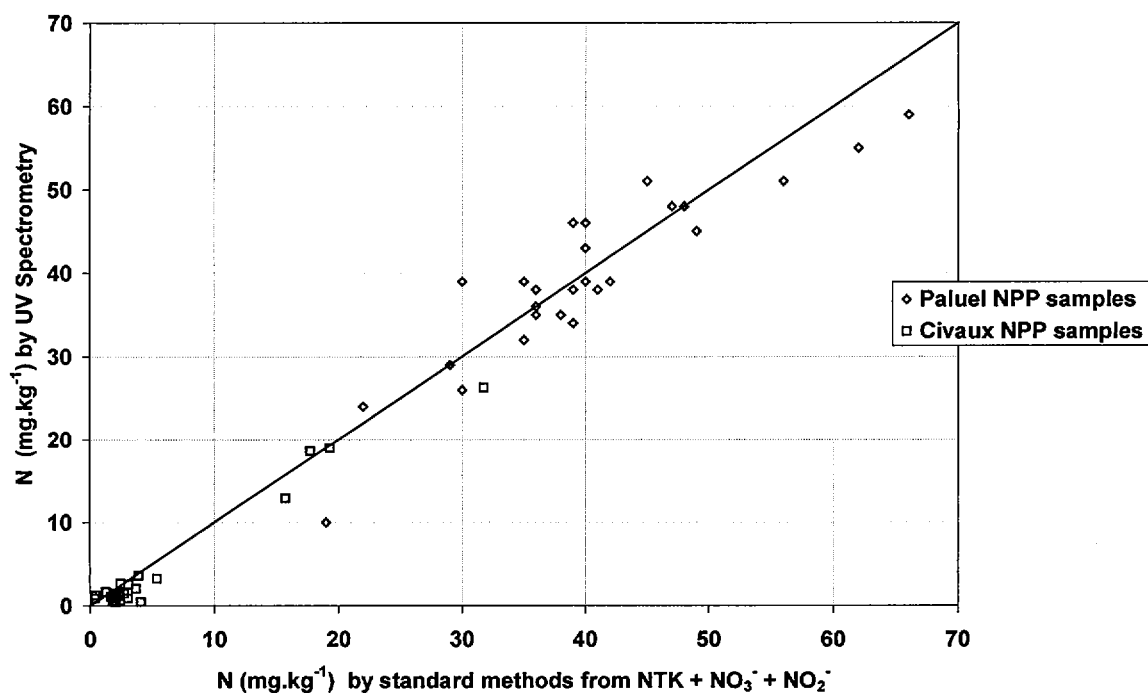


Figure 7 : Correlation between N measured by UV spectrometry and standard methods on liquid waste

Moreover, the UV spectrometry analysis presents the advantage of being faster (30 minutes instead of 4 hours for conventional methods) and safer in the case of total nitrogen determination. The UV spectrometry apparatus also enables to develop similar methods to measure surfactant, phosphate and COD.

As the new ministerial order specifies many more chemical controls, the NPP laboratories need reliable, simple and easy to use methods such as UV spectrometry. EDF also studies the capillary electrophoresis technique applied to the determination of amines and metals, as this multi-parameters method presents the same advantages as UV spectrometry.

4. CONCLUSION AND PROSPECTS

The new waste release control in French NPP is more restrictive than the old one and needs heavy investment to bring plants to compliance with it. The great evolutions are a chemical follow up on more chemicals with a higher measurement frequency and with lower maximum concentrations and a specific measurement of carbon 14. Regarding radioactive releases, a new counting has been settled and activity of carbon 14 release is now measured and no longer calculated. The evolution of the French regulation leads to develop specific procedures and analytical techniques in chemistry and in radiochemistry (UV spectrometric methods, carbon 14 measurements, ...)

EDF NPP operators have launched a voluntarist process to reduce their-releases since the beginning and before the evolution of the regulation. EDF priorities in terms of environment care lead henceforth to implement a global optimisation of the impact for a better control of releases. The new regulation will help EDF to reach its goals because it covers all the aspects in one administrative document: it is seen as a real simplification and a clarification towards public. In addition, this new regulation fits in with international practices which will allow an easier comparison of results between EDF and foreign NPP.

These big environmental concerns lead EDF to create a national dedicated laboratory (LAMEN) in charge of developing specific measurement procedures to be implemented either by NPP or by sub-contractor laboratories.

Currently, the PWRs concerned by the new control are Saint-Laurent, Paluel, Flamanville, Belleville, Saint-Alban and more lately Chinon and Cruas. From now to 2006, all EDF NPP will be concerned.

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