

IDENTIFICATION AND REMOVAL OF ORGANIC POLLUTANTS FROM JRC-ISPRA HEAVY WATER: LAB-TESTS FOR THE DESIGN OF ON-SITE PURIFICATION PROCESS

Authors: Mario Mariani, Francesco Maluta, Marco Giola
Dipartimento di Ingegneria Nucleare - CeSNEF, Politecnico di Milano,
via Ponzio 34/3 – MILANO, Italy

Roberto Covini, Sergio Bertelli, Giuseppe Bielli
European Commission, Joint Research Centre Ispra,
via Fermi 1 - 21020 ISPRA, Italy

Abstract

Unexpected high values of Total Organic Carbon were found in some stocks of slightly tritiated heavy water before their shipment from JRC-Ispra to the future owner.

Due to the radioactivity of the water, compatible tests and chemical investigations were performed to identify the organic pollutant/s supposed to be present in the samples. UV-VIS and GC-MS measurements showed that acetone was the principal responsible of the organic pollution. In order to individuate a suitable method to remove pollutants from the bulk, several laboratory investigations were carried out on cold tests solution with different absorption systems.

The best results for total removal of acetone from water were obtained with absorption on a column charged with microporous activated carbon (GAC) supplied by Norit[®]. The optimized parameters (geometry, volume, carbon amount, flow-rate/contact time, etc.) were transferred from lab- to plant-scale.

The details and the results of the laboratory investigations are presented in this paper, while the bulk operations concerning the treatment of about 46.000 kg of slightly tritiated heavy water have been given in another paper¹.

This paper outlines the analytical approach and the strategy used in identifying and removing an organic pollutant from JRC-Ispra heavy water. The good results obtained in a lab-scale encouraged to apply the purification technique tested to the real study case, where the performance has been optimal.

Analytical Procedures

During the re-drumming operations, a number of samples was taken from each lot of tritiated heavy water. In order to minimize the risks of sampling operations, a sampling point was arranged in the mobile purification equipment, after the ion-exchange resin bed.

The cock was provided with a stainless steel needle in order to sample directly into a screw-top glass bottle, under vacuum, sealed with open-top screw-cap and PTFE-faced silicone septum. All sampling bottles (250 or 500 ml) and screw-caps, have previously been pre-clean, conditioned and dried and deuterated, as requested.

Sealed sampling bottles were moved to the chemical analysis hot lab within the INE Pool area.

¹ Covini R., Bertelli S., Bielli G., Mariani M., Maluta F., Giola M., “The System for the Collection, Purification and Re-drumming of the Heavy Water at the JRC-Ispra: Design, Operation and Implementations”, 2003.



Figure 1. The analytical glove box

Each sample was analyzed measuring the seven quality parameters, which are indicated in Table 1, with their acceptance limits.

	Parameters	Acceptance limits	Analytical method
1	D ₂ O isotopic abundance	99.5% wt	IR Spectrophotom. / Densitometric
2	Electrical conductivity	2 μ Sm/cm	Conductimetric
3	pH	6.5 - 9.5	Potentiometric
4	Total Organic Carbon	1.1 mg/l	UV-VIS Spectrophotometric
5	Oil	1.1 mg/l	IR Spectrophotometric
6	Turbidity	2 NTU	Nephelometric
7	Tritium activity	11 Ci/l	Liquid Scintillation

Table 1. The quality parameters, their acceptance limits and the analytical methods.

Each measuring procedure and the techniques have been studied for reducing any contamination risk, during the manipulation and analysis, considering also the contribution of possible isotopic exchange for tritium with atmosphere and hydrogenated materials.

The **isotopic abundance** was measured on a infrared spectrophotometer, examining the O-H stretching line at 3400 cm^{-1} (for samples having a title higher than 99.5% wt) or densitometrically in the other cases. The cell preparation and filling was operated in a special anhydrous pressurized glove box, using PTFE or glass tubing and CaF₂ cells for liquids.

The technique chosen for the determination of the **total organic carbon** permitted to avoid contamination of the TOC analyzer instrument (which heats the sample to vaporization), using a spectrophotometric method. A small amount of sample (2 ml) was pipetted in a sealed glass vial containing a predetermined amount of oxidating agent (persulfate ion); the oxidation reaction took place in the vial during the hot digestion treatment and the result was obtained measuring the absorbance at a specific wavelength, inserting the vial in a UV-VIS photometer. The main advantages of this procedure are the safe and complete sealing of the radioactive solution and the small equipment needed in the analytical lab instead of the traditional analyzer.

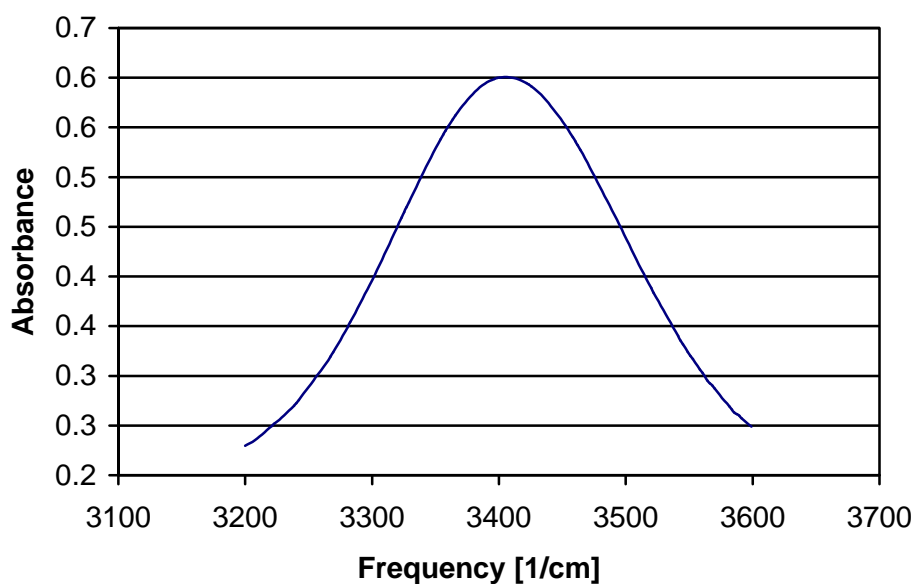


Figure 2. The IR spectrum of a heavy water sample. The peak around 3400 cm^{-1} allows to calculate the exact isotopic composition of heavy water samples.

The analytical D_2O lab was completely refurbished with two glove boxes, vacuum furnace, air and N_2 lines, an infrared (IR) and UV-VIS spectrophotometer and other portable instruments (nephelometer, conductimeter, ...). Sample handling was carried in a wheelable glove box, which has been modified and connected to the off gas vent system. During analytical operation, an auxiliary ventilation system was operated in order to guarantee adequate safety for operators. During all the operation time no contamination, liquid pouring or leakages were detected and the tritium level in the chimney was well under limits.



Figure 3. The anhydrous glove box for IR sample preparation.

Troublesome analytical data during quality checks

During the re-drumming operations of the various lots, the critical parameters indicating water quality were periodically measured. Unsuspected problems arose from high Total Organic Carbon (TOC) values encountered for the second stock (A1). The TOC values, despite several repetitions, was well above the acceptance limit (1.1 mg/l – see Table 1) and indicated the presence of some organic contaminant. At the same time, the positive answer of the Chemical Oxygen Demand (COD) test, which is related also to the presence of organic carbon, gave a confirm for some uncompliances of the heavy water. The re-drumming operations were stopped as soon as possible, and it was estimated necessary to proceed in further investigations in order to discover the nature of the pollutant.

Identification of the extraneous contaminant

Some interviews have been conducted between the personnel in charge during the first drumming in 1985 (as no written records were available). It was discovered that, before filling operations, the drums were prepared with several consecutive washings: detergent solutions, rinsing water to clean from residual soap and, finally, acetone to eliminate residual water. After all, each drum was air dried.

Since the data gathered from the other parameters were in conformity with buyer's requirements and extracted oils represented a negligible contribution to TOC and COD, our attention focused on organic solvents. Furthermore, COD/TOC ratio measured in several contaminated samples was always about 4, in good agreement with stoichiometric calculations, accounting for a possible acetone presence. Considering the radioactivity of the water, it was decided to proceed with a simple colorimetric test for ketones (a reaction with 2,4: dinitrophenylidrazine)², which had a positive response, but did not permit to evaluate the concentration of the pollutant, as the results were above the limited linear concentration range of the test. A second trial was done, deciding to conduct a GC/MS test over the head space of a stoppered vial containing a few mL of heavy water, in order to reduce the presence of radioactivity in the vapour phase. During the heating (about 70°C), all the organic (low boiling point) substances would be transferred for the most part to the vapour phase, while tritiated heavy water should have remained in the liquid phase. In Figure 4 are reported some GC/MS spectra. The results of the measures clearly indicated that the incriminated molecule was acetone and the quantitative analysis showed a concentration ranging from 40 to 50 mg/L (ppm) into the samples checked, according with TOC and COD results.

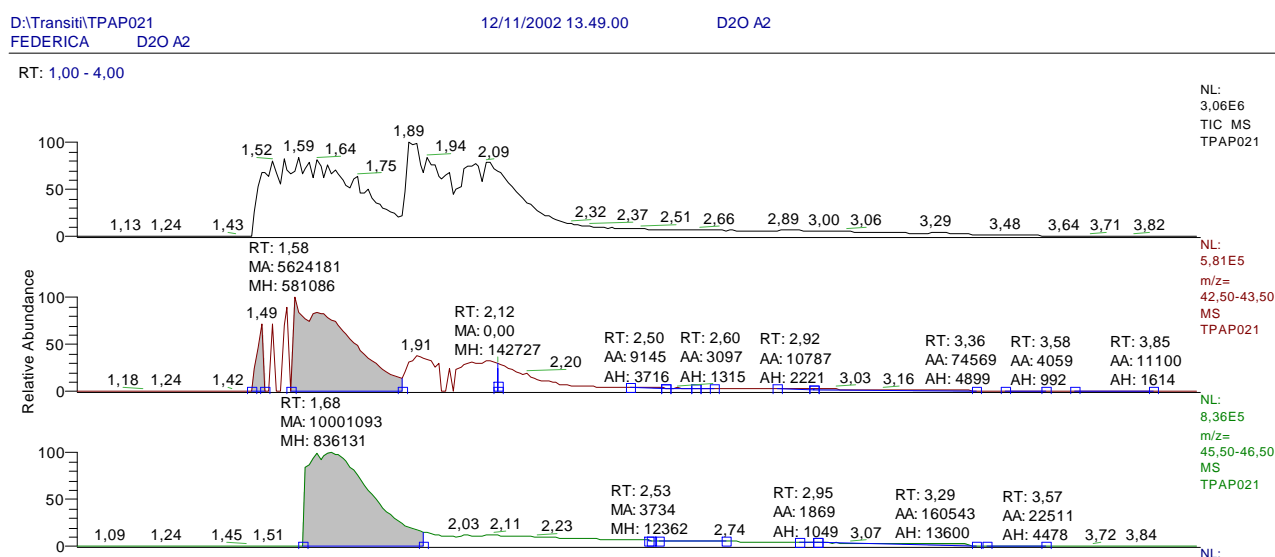


Figure 4. Mass spectrometry report (line 1: total; line 2: m/z = 43; line 3: m/z = 46)

² Vogel A.I., in "Practical Organic Chemistry", Longman, 1948.

The results of the mass spectrometry also revealed a striking isotopic effect: the atomic masses of the ions detected can be accounted for deuterated acetone where hydrogen atoms have been substituted by deuterium ones (Table 2). Infact the area for the m/z ratio 43 (non deuterated fragment ion) is $5 \cdot 10^6$, while the area for m/z 46 (completely deuterated ion) is 10^7 .

Fragment ions		CH ₃ COCH ₃	CD ₃ COCD ₃
CH ₃ ⁺ E	m/z	15	18
C ₂ H ₃ ⁺ E		27	30
CH₃CO⁺E		43	46
M ⁺ E (molecular ion)		58	64

Table 2. m/z ratios for acetone's fragment ions. The CH₃CO⁺ ion determination is reported in Figure 4.

A practical solution to heavy water pollution

Finding an unsuspected organic pollutant during the re-drumming operations for the first shipment of heavy water suggested to take precautionary steps for the re-drumming of the second shipment. As the pollution seemed to be accidental, it could not be excluded a certain variability in the pollutant concentration.

Considering the possibility of having twenty tonnes more of water not responding to the buyer's specifications, it was decided to study a purification process for the remaining heavy water.

The treatment should satisfy the following requirements:

- Effective in acetone removing
- Capable of a generic purification towards other possible organic contaminants (i.e.: terphenyl, hydrocarbons, etc.)
- Be flexible and modular
- Safe and reliable (no servicing to contaminated parts, no spilling...)
- Minimum amount of radioactive waste produced
- Economic

The commercial solutions adopted for potable water or sludge purification were screened. Amongst the various possibilities, considered the low boiling point of acetone (56.1°C), stripping is generally adopted in similar cases. But, as this solution was clearly unfeasible for the tritium release generated in such a treatment, a solid state physical adsorption system was surveyed. The advantages connected to solid state adsorption are: feasibility and easiness, no limit in the pollutant concentration to be treated, the non specific adsorbing capacity for every possible contaminant and, last but not least, economicity.

All the preliminar tests were carried-out in the Radiochemistry Laboratories of Politecnico di Milano, using a synthetically contaminated water, prepared by spiking high purity water with acetone to the concentration measured in the real radioactive samples.

A screening of the adsorbing capacity of various matrices towards acetone, showed significative differences in the results of COD test carried on water samples containing acetone (50ppm) after conditioning with different adsorption media (see Table 3).

MATRIX	Relative yield
ZEOLITE 13X	-0.57
GAC 1240 (Mesoporous)	0.40
GCN 1240 (Microporous)	1.00

Table 3. Comparison of different solid adsorbents in removing comparable amounts of acetone

The results of the GCN Carbon, which showed the best performance, are supported on the basis of the physical nature of this adsorbent. Infact, the GCN coconut carbon has a microporous structure suitable to guest small molecule like acetone.

However, acetone is not the ideal molecule for a physical adsorption treatment: the polarity pulls the molecule to assume an hydrophilic solvated state which is unlikely to be adsorbed on carbon. Furthermore, this is a small and light molecule; generally, the carbon pores are most likely to trap bigger and heavier molecules: Table 4 shows the adsorptive capacity of an activated carbon (Filtrisorb 400) towards ketones of increasing atomic weight or, from a different point of view, molecules of growing steric hindrance (see Figure 5).

Compound	M _w	Adsorptive Capacity X [mmol/g]
Acetone	58.08	0.05
Methylethylketone	72.11	0.18
Diethylketone	86.14	0.43
Methylisobutylketone	100.16	0.75
Ethylbutylketone	114.19	1.54

Table 4. Adsorptive capacity of Filtrisorb 400 Activated Carbon towards ketones with growing molecular weight³

By the data obtained in Table 3, It seems evident, at this point, that a microporous coconut carbon is needed to optimize the acetone adsorption. Many batch cold tests were carried out in order to verify the adsorption behaviour of GCN 1240 towards acetone, which has no references in literature.

It is to be underlined that the choice of an activated carbon has a further advantage: due to the strong oxidation process of activation, the carbon contains practically no hydrogen, in view of facilitating decontamination from tritium.

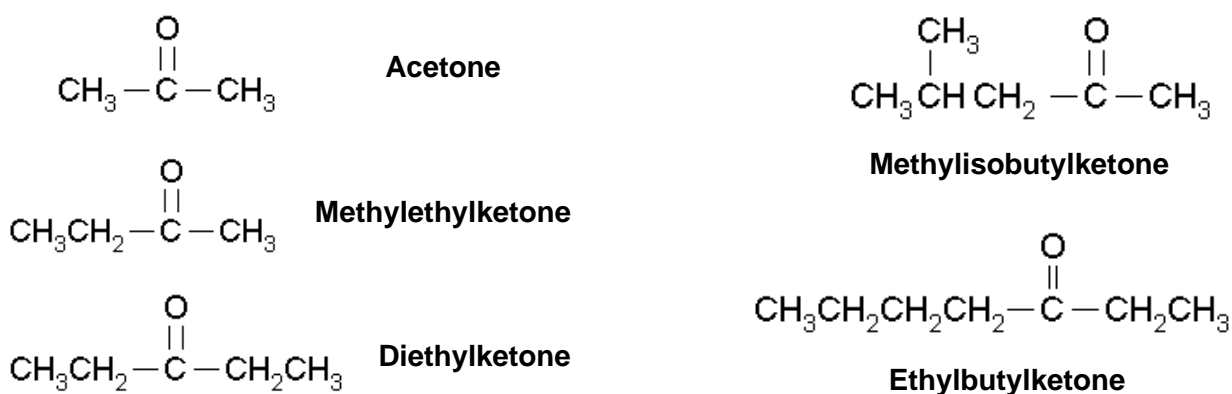


Figure 5. The growing molecular weight of the ketones family corresponds to lengthening carbon chains.

Determination of the adsorption isotherm (batch tests).

The adsorption isotherm curve was drawn from many experimental points, following the 3860 ASTM (*Standard Practice for the Determination of the Adsorptive Capacity of Activated Carbon by Aqueous Phase Isotherm Technique*). The primary goal of these tests was the identification of the ultimate capacity of carbon for this contaminant.

Equilibrium adsorption behaviour behaves as a Freundlich type isotherm law:

$$X = K C^{1/n}$$

Where: X = constituent adsorbed for unit weight of carbon

³ Arbuckle W.M., "Estimating Equilibrium of Organic Compounds on Activated Carbon from Aqueous Solutions", in *Env. Sci. & Tech.*, **1981**, *15*, 812-819.

C = concentration of constituent remaining after treatment
 K & n : empirical factors

As this curve tends asymptotically to zero adsorbent loading at low concentrations, it is important to evaluate the feasibility of the treatment measuring the practical minimum residual concentration of the selected component in liquid phase. If this limit satisfies the maximum concentration admissible for treated water, the process is possible. Batch tests have proved the minimum residual concentration to be lower than 3.5 mg/l (ppm of acetone), which has been reputed acceptable.

The second part of the batch test campaign was directed to measure the ultimate capacity of the carbon for the adsorbate, that is the amount of impurity adsorbed when the carbon is in equilibrium with the influent concentration (Table 5). These data were needed to project the absorption treatment plant, calculating the mass of carbon needed to process all the heavy water volume.

	GCN 1240	Filtrisorb 300
Effluent minimal concentration [mg/l]	1.1	3.29
Equilibrium adsorption capacity [mg/g]	12.31-15.94	8.47

Table 5. Comparison between data obtained with GCN 1240 in batch tests and literature data for Filtrisorb 300 Activated Carbon³

Also physical properties of GCN 1240 Norit Activated Carbon have showed to be definitely superior (Table 6). In particular, the outstanding hardness minimizes the crushing effect of flow friction, which can lead to increased pressure drop and interfere with the operation of the column.

Physical Properties	Unit	S 51 FF Darco (in ACF 07)	Filtrisorb 300 8-30 Calgon	GCN 1240 Norit
Internal Surface Area (BET-Dry Basis)	m ² /g	650	950-1050	1150
Total Pore Volume	cm ³ /g	1.0	0.85	0.8
Apparent Density	g/cm ³	0.45	0.48	0.51
Abrasion Nr. (Hardness)	-	n.d.	70	95
Ash	% wt.	n.d.	8	3.5

Table 6. Physical properties of some typical commercial Activated Carbons types

Small scale lab treatment (column tests)

The second step implied the realization of a small scale column test, simulating the adsorption of the target compound on GAC in a large column or full scale adsorption application. The experiments were employed for the determination of breakthrough curves for specific contaminants in water and the length of the adsorbates Mass Transfer Zone (MTZ), where the exchange capacity is lower than the optimal one. Following the 6586 ASMT (*Standard Practice for the Prediction of Contaminant Adsorption on GAC in Aqueous System Using Rapis Small Scale Column Tests*), a glass column, packed bed height 1 m, was manufactured with five PTFE sampling cocks. A small test apparatus was arranged with a zero headspace reservoir for the feed water spiked with acetone, a peristaltic pump for the optimal flow rate regulation to constant diffusivity conditions and the activated carbon column (the system is illustrated in Figure 6).

The filling of the column was conducted with particular attention to tight packing of granular activated carbon, avoiding air bubbles, which could result in flow troubles. The conditioning of the column was carried on with high purity water first in countercurrent flow, in order to lift all the carbon dust to the top of the column and remove any air bubble, then from top to bottom flowing until conductivity and COD of outflowing water was equal (or lower) to the feed water.

Finally the tests with the spiked solutions simulating the real contaminated water were carried out measuring the volume processed (at constant flow rate) and the COD (that was chosen as check parameter) at the various sampling points.

The reasons for choosing COD were the simplest realization of the cuvette tests (with reduced times for the analysis), the wider range of measurement and its safe and prompt application to the real radioactive waste.

The experiments confirmed the effectiveness of this method for removing almost completely the polluting substance (less than 1 mg/L remaining).

Figure 7 shows that the breakthrough point is situated at half of the bed height, reducing the total loading capacity for the target contaminant to half of the theoretical value.

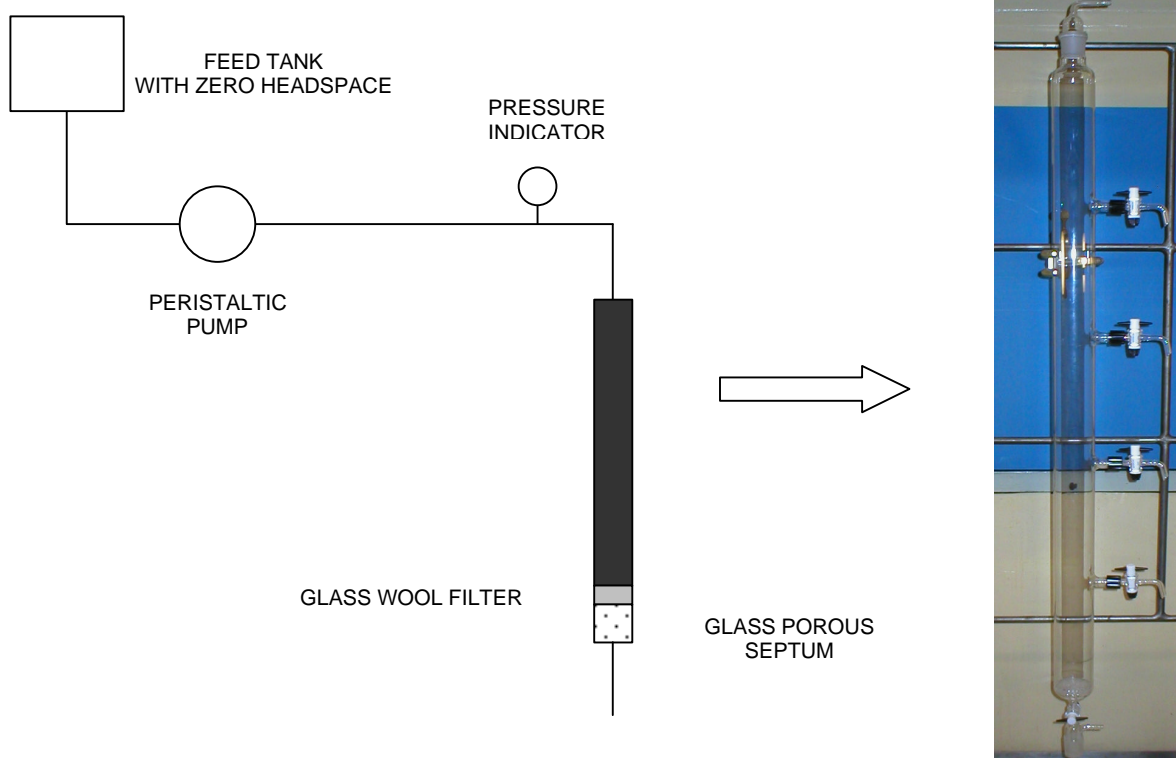


Figure 6. Scheme of the test apparatus.

At the right end, a picture of the glass column before filling operations.

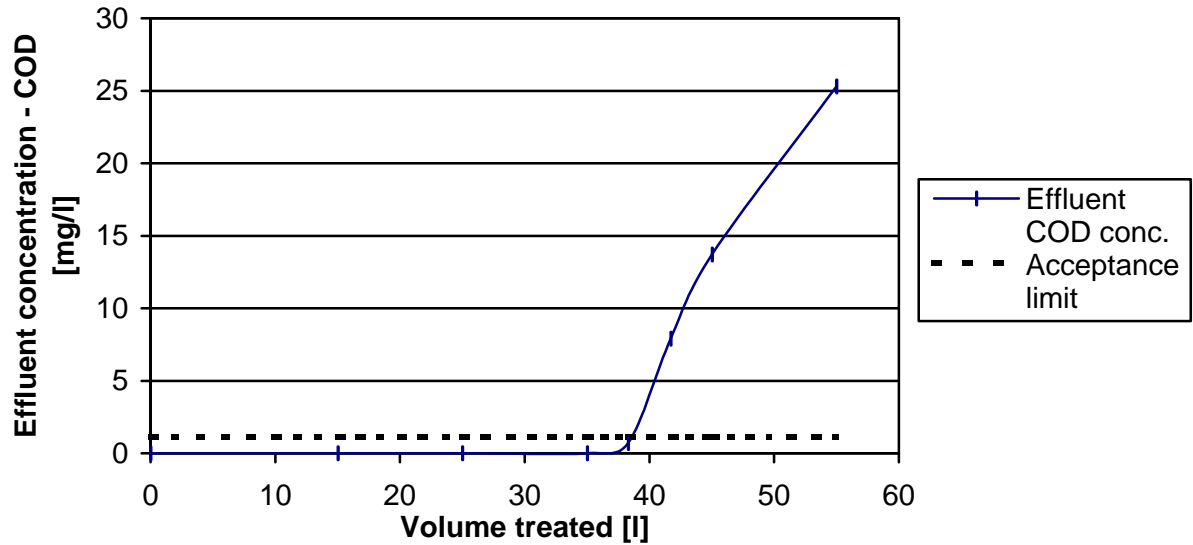


Figure 7. The breakthrough point of the column is situated at approximately half its bed height. The volume of fluid processed is 35 out of 60 litres that should have been treated applying the theoretical equilibrium capacity.

The global efficiency of the carbons occurring to remove acetone could be considered poor, if compared to normal operating conditions for a waste water purification plant. However, in this case, the small volume to be treated (just 20000 litres), the feasibility of this solution adopted with tritiated water and the low cost, suggested to add an activated carbon filter to the existing mobile purification equipment¹. The data from the test illustrated have been employed to size the activated carbon filter to put in the heavy water drumming circuit, after the resin's vessels. Considering 20 tons of water to be processed, supposed having a 50 mg/l concentration in acetone, it was estimated a quantity of about 140 kg of activated carbon, which has been packed in a standard stainless steel (AISI 304) barrel (height 1430 cm, diameter 700 cm).

Aknowledgement

The authors would like to thank Dr. Luigi Besozzi and Norit Italia S.p.A. for the precious contribution and technical advice in the Activated Carbon tests.