

# Accidental spills: the C.E.C., a new device to test

## initial dissolution rate of chemicals in seawater column.

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### Abstract

*In this paper we describe a unique tool, The Cedre Experimental Column – a 5 m-high seawater column–designed to estimate, under specific conditions of temperature and salinity the initial dissolution rate of floating or sinking chemicals spilled at sea. Owing to kinetics of solubilisation, this parameter seems more operational than solubility limit, the only solubility parameter available in the literature. Moreover, this parameter is seldom documented in conditions of temperature and salinity specific to seawater.*

*The device was designed to allow rapid implementation. In conjunction with a software it will give the authorities in charge of emergency situations a mean to evaluate and anticipate the evolution of a spill and then act efficiently after an accident involving a chemical which interaction with seawater is poorly documented.*

*Device and procedure have been tested on selected chemical compounds in a range of density and water solubility.*

### Keywords

Cedre Experimental Column (C.E.C.); oil spills; chemical spills; initial dissolution rate

### 1. Introduction

One of the consequences of the increasing global economy is the continuous development of the international maritime transport. For instance, from 1970 to 1995, the maritime transaction of chemicals sharply increased by 270% (Cedre, 2000). In the English Channel, the shipping traffic increased from 30 million tonnes in 1989 to 150 million tonnes in 2000 (Mamaca, 2003). One of the downsides of this intensifying traffic was the occurrence of numerous accidents, such as the sinking of the *Ievoli Sun* on October 31<sup>st</sup>, 2000 in the English Channel. This vessel contained 3998 tonnes of styrene, 1027 tonnes of 2-butanone and 996 tonnes of 2-propanol. She sank at 49°52'5N 2°23'7W, about 11 miles northwest of Alderney in 70 m-deep water (Law, 2003). Moreover, her tanks leaked. 2-Propanol is fully miscible with water and 2-butanone relatively miscible, while the solubility of styrene is very low. As a consequence, in case of breaking tanks, 2-propanol and 2-butanone would be dispersed and diluted throughout the water column and

could be responsible for toxic effects on the pelagic fauna. Styrene would on the other hand rise to the sea surface and evaporate, which would result in human exposure (UNEP, 2006). This accident and others, at sea (Ece, 2005 (Cedre, 2006)) or not (Benzene release in Song Hua River, China, 2005; (Cedre, 2005; UNEP, 2006; Ambrose, 2006)) showed that not all the required information can be found in the literature and that studies have to be undertaken i) to forecast the behaviour of chemical products in the environment and ii) to plan rapid intervention in case of an accident.

As a matter of fact, it is essential that emergency officers understand the fate of compounds at sea, for efficient and rapid action. During the *Ievoli Sun* response process, a key point was to estimate the quantity of styrene that could be found at the sea surface, as well as the gas cloud volume. This knowledge was necessary i) to determine the risk of air pollution, ii) to control the traffic above the wreck, and iii) to assess the risk of a toxic gas reaching the shoreline.

The dissolution rate of chemicals i) must be distinguished from solubility limit which is a thermodynamic parameter, ii) can be defined as a mass transfer of a chemical (organic phase) into water (aqueous phase) over a period of time, or during a flow process. The intensity of this transfer depends on environmental factors (temperature, pressure, salinity), on the initial conditions of the experiment (injection speed) and on the chemical itself (Giovannacci, 2002). In numerous situations, initial dissolution rate is the most pertinent parameter among those involved in solubilisation processes. To study the initial conditions of solubilisation, the behaviour of any chemical was studied by observing droplet flows in a seawater column. The method consisted in determining the variation in volume of droplets between two depths, using a video acquisition and treatment system.

If an isolated droplet is spherical, it will be distorted to an ellipsoidal shape when subjected to different strengths, such as gravity and interfacial strengths (Danmoto, 2004). Models of droplet behaviour have been established, assuming such a shape (Wu, 2002). Local pressures on a droplet (e.g. whirlpools) and speed variations relative to the continuous (aqueous) phase can be responsible for some oscillating movements of the droplet. This can result in droplet collisions followed by their coalescence (Giovannacci, 2002), but droplets can also be broken when the kinetic energy exceeds the surface energy (White, 2000; Simon, 2003).

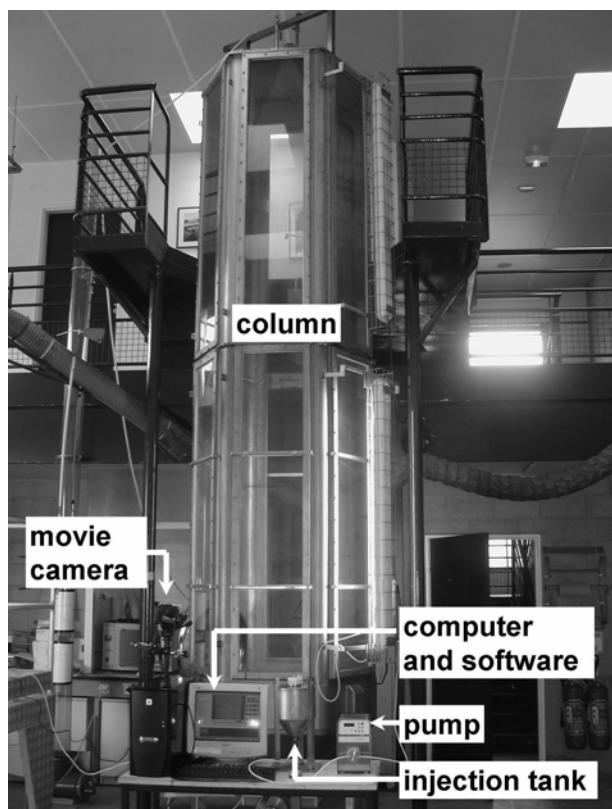
All these phenomena must be taken into account to analyze the droplet flow and behaviour.

As an organization specialized in operations in case of accidental water pollutions, *Cedre* (Centre of Documentation, Research and Experimentation on Accidental Water Pollution) invested in a unique tool: the *Cedre* Experimental Column (C.E.C.). The C.E.C. is a hexagonal five-meter high column which can be used to simulate and visualize the behaviour of chemicals during their flow in a vertical water column. The development of a method to determine the initial dissolution rate of compounds using the C.E.C will be explained below.

## 2. Materials and Methods

### 2.1 Experimental setup: The *Cedre* Experimental Column (C.E.C.)

The C.E.C. is a hexagonal five-meter high column of which only three meters are of use for measurements (Figs 1 and 2). The hexagonal shape was chosen because it provided both better resistance than a parallelepiped and better optical properties for video observation than a cylinder.



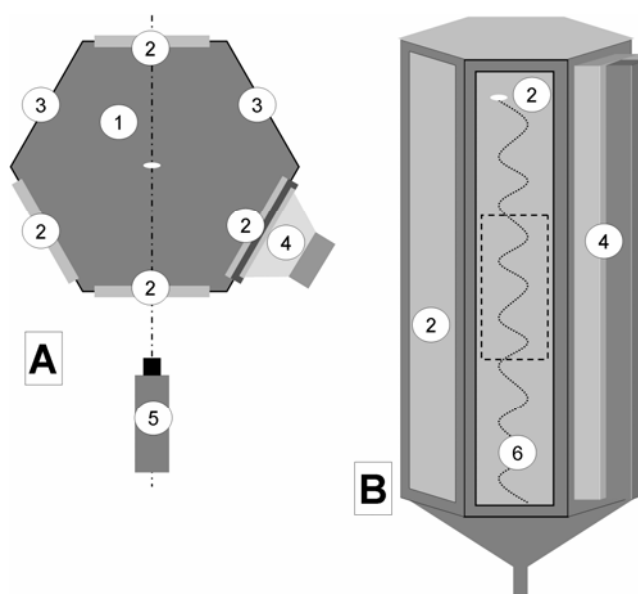
**Fig. 1:** The *Cedre* Experimental Column (C.E.C.) and its tools.

Opposite sides are 0.8 meter from one another, leading to a column volume of 2770 L. The column is made of stainless steel (type 316L). Four 16 mm-thick glass windows allow the droplet behaviour inside the column to be observed under cold white light. The bottom of the column is conically shaped in order to isolate either

sinking or floating not dissolved chemicals before or after emptying the column, respectively. The remaining seawater containing dissolved chemicals with concentrations lower than the toxicity limits was stored in a settling pool complying with ISO 14001 standards.

The C.E.C. is usually filled with seawater which can either remain in the column throughout one experiment, or be renewed. Nine valves are placed every 50 cm along the vertical axis of the column in order to sample seawater at various depths. To filter gas emissions and to maintain the water surface under atmospheric pressure, the top of the column is connected to a fume hood.

An injection system can be attached at the top or at the bottom of the column to inject chemicals, depending on their specific mass (higher or lower than the seawater one), with a well defined flow. In each experiment, 2.5 L of chemical were injected.



**Fig. 2:** Scheme of the *Cedre* Experimental Column (C.E.C). Horizontal section (A) of the column with the camera position; outside of the column, with droplet movement. 1. Seawater inside the column; 2. Glass sides; 3. Opaque sides; 4. Cold white lights; 5. Digital video camera on tripod; 6. Helicoidal droplet movement up the column.

### 2.2 Video system and procedure

A video camera (Sony – DCR-TRV8), with Videostudio 7 (software distributed by Ulead) was used to capture and register all videos of droplet flows. The camera was placed in front of a window at a distance of about 10 cm and then focused on a 3-m test pattern used for calibration of both camera and software. Graduated in centimetres, it was placed along the vertical axis inside the column right under the seawater surface so that the “zero” of the test pattern corresponded to the surface level. It pictured a 10 cm × 10 cm field in which the droplet dimensions were measured, assuming that the droplet volume did not change during this 10-cm path.

### 2.3 Conditions of droplet formation and observation

Droplets were formed near the injection aperture. However, in this zone, the shape variations were important. So, the "initial" droplet dimensions were determined 15 cm away from the injection aperture. To determine the dissolution rate, it was necessary to record another droplet flow at another depth. The determination of the second depth depended on the dissolution capacity of each product. When the product was highly soluble, droplets were observed 1 m above (or below) the first position, whereas this distance increased up to 2.5 m for the least soluble compounds.

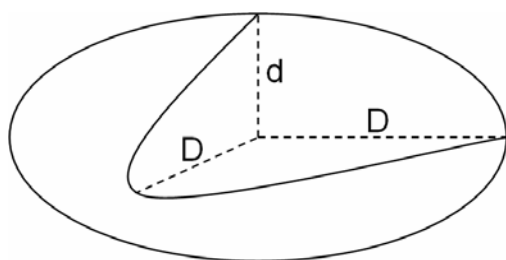
Droplet positions were noted  $P_0$  for injection depth, and  $P_{\pm h}$  for a droplet located  $h$  centimetres above (+ sign) or below (- sign)  $P_0$ .

After injection of the chemical, a 30-s video of the droplet flow was filmed at each depth previously defined, at a rate of 25 frames per second. For analysis, every film was cut into separate  $720 \times 576$ -pixel pictures in order to determine the surface and the volume of each droplet.

Visual observations showed that droplets had a flattened ellipsoidal shape (oblate) with a vertical axis of symmetry. It has also been shown that in ascending or descending movements, the droplet path was not linear but rather helicoidal (Ellingsen, 2001). So, the "camera-to-droplet distance" was slightly varying and droplets sometimes moved away from the focal plane. Therefore, the blurriest images had to be eliminated before further analysis to obtain coherent results.

Virtual dub software (distributed by Avery Lee) was used to deinterlace every video while Aviméca (distributed by Microsoft) was used to analyse droplet dimensions at each still in video sequences.

After software calibration with the test pattern video, Cartesian coordinates of four characteristic points (Fig 3) could be determined for each droplet, leading to the determination of their minor ( $d$ ) and major ( $D$ ) axes.



**Fig. 3: Oblate ellipsoid parameters: minor ( $d$ ) and major ( $D$ ) axes.**

Therefore, the apparent surface ( $S_a$ ) of the droplets could be calculated and used for two tests: first, to determine the number of stills to analyze, then to determine the number of droplets to analyze to obtain statistically significant parameters. Furthermore, the volume ( $V$ ) and the actual surface ( $S$ ) of the droplets were calculated using formulae (1) and (2):

$$V = \frac{\pi}{6} d \cdot D^2 \quad (1)$$

$$\text{and } S = \frac{\pi D}{2} \left( D + \frac{d}{2e} \times \ln \left( \frac{1+e}{1-e} \right) \right) \quad (2)$$

where  $e = \sqrt{\frac{D^2 - d^2}{D^2}}$  is the eccentricity.

The Shapiro statistical test was used in order to check the normality of the observed distribution (Shapiro, 1965).

### 2.4 Chemicals

The chemicals studied in this project and some of their physicochemical parameters are listed in table 1. The seawater (salinity  $27 \text{ kg m}^{-3}$ ) was pumped from Brest harbour, filtered and UV-treated before use. The mean water temperature during the experiments was  $18^\circ \text{C}$ .

**Table 1: specific mass, solubility, viscosity of chemicals under study.** Specific masses in  $\text{g cm}^{-3}$  and viscosities in  $\text{mPa s}^{-1}$  are given at  $18^\circ \text{C}$  while solubility limits are in  $\text{g L}^{-1}$  at  $20^\circ \text{C}$ . Data are from: Acros Organics and \* INRS (French National Institute for Research and Security).

Chemical	Mass density	Solubility	Viscosity
Styrene *	0.91	0.3	0.75
1,2-Dichloroethane *	1.26	8.7	0.84
Ethenyl acetate	0.93	23	0.43
2-Methoxy-2-methyl-propane	0.74	51	0.36
2-Propenenitrile	0.81	73.5	0.35
Hexanedinitrile	0.96	90	6.66
2-Methyl 1-propanol	0.80	95	4.09
2-Methyl 2-butanol	0.81	120	5.19
2-Butanol	0.81	125	4.40
2-Acetyloxyethyl acetate	1.11	160	2.97
2-Butanone *	0.81	290	0.43

### 2.5 Experimental parameters

**Optimal injection flow:** The injected droplets must have similar sizes and be spaced enough to limit interactions between successive droplets. As a matter of fact, when the injection rate was too low, droplets were injected irregularly with a random volume, while an excessively high injection rate increased the injection frequency of the droplets and consequently the likelihood of droplet interactions. This led to the determination of an optimal injection rate for every chemical (Table 2).

**Table 2: Optimal injection flow for each chemical.**

Chemical	Optimal injection flow (mL min <sup>-1</sup> )
Styrene	6.5
1,2-Dichloroethane	10.1
Ethenyl acetate	30.0
2-Methoxy-2-methyl-propane	32.0
2-Propenenitrile	29.5
Hexanedinitrile	10.1
2-Methyl 1-propanol	10.0
2-Methyl 2-butanol	6.6
Butan-2-ol	7.0
2-Butanone	22.7

**Droplet speed:** The average time necessary for a droplet to travel over a distance of 1.2 m was measured in order to determine the flow speed.

**Mean droplet initial volume:** For each chemical compound and each injection rate, the number of droplets injected per minute was counted. Therefore, knowing the chemical injection flow and the droplet injection frequency, the mean volume of the injected droplets could be evaluated and compared with the one determined by image treatment.

1,2-Dichloroethane was used to compare both methods.

Three countings were done for two different injection rates (7.9 and 10.1 mL min<sup>-1</sup>), giving the same results.

Given the low solubility of 1,2-dichloroethane in water (8.7 g L<sup>-1</sup>), the droplet volume did not vary during their flow between P<sub>0</sub> and P<sub>15</sub>. So, the initial volume was calculated at P<sub>15</sub> where the droplet shape was checked to be ellipsoidal.

Table 3 shows that the droplet volume difference between both methods was lower than the uncertainties on the values calculated from image treatment. Thus, the assumption made on the droplet shape was satisfying, and droplets can actually be assimilated to ellipsoids.

**Table 3: Initial volume of 1,2-dichloroethane droplets estimated using M<sub>1</sub> and M<sub>2</sub>.**

Injection flow (mL min <sup>-1</sup> )		7.9	10.1
Number of droplets injected per minute		134	162
Mean volume of droplets (mm <sup>3</sup> )	Counting at P <sub>0</sub>	58.7	54.7 ± 4.3
	Image treatment at P <sub>15</sub>	62.3	61.9 ± 3.1

### 3. Results and Discussion

#### 3.1 Determination of the minimum number of stills and droplets to analyze in order to obtain statistically correct parameters

The mean dimensions were calculated in two steps: first, the apparent dimensions of ten droplets were calculated; then, the homogeneity of these measures was

checked using the Shapiro-Wilk test (Shapiro, 1965) and the parameters corresponding to a droplet population could be determined.

**Determination of the number of stills to analyze in order to calculate the apparent dimensions of one droplet.**

The test was done in the case of styrene. The droplet dimensions were measured at P<sub>+15</sub>, for an injection flow of 6.5 mL min<sup>-1</sup>. The mean apparent lengths of the axes (D, d) were measured, considering ten (I<sub>10</sub>) and forty (I<sub>40</sub>) stills. Table 4 shows that there hardly exists any discrepancy between I<sub>10</sub> and I<sub>40</sub>. Therefore, throughout the 10-cm droplet flow, only ten stills had to be analyzed to determine the mean apparent dimensions of one droplet.

**Table 4: Comparison of the averaged apparent dimensions of styrene droplets, calculated considering 10 or 40 stills.**

	d (mm)	D (mm)	S <sub>a</sub> (mm <sup>2</sup> )
I <sub>40</sub> (n=40)	9.5	13.7	102.2
I <sub>10</sub> (n=10)	9.7	13.5	102.8
Variations	2 %	1.5 %	0.5 %

**Determination of the number of droplets required to calculate the apparent dimensions of a droplet population at a specific depth – Shapiro-Wilk test**

The Shapiro-Wilk test:

To check the homogeneity of the axis length and apparent surface measurements, it was important to show that they exhibited a Gaussian distribution. This was demonstrated using the Shapiro-Wilk test (Shapiro, 1965). It consists in calculating a value W and comparing it to a critical value W<sub>crit</sub>. If W < W<sub>crit</sub>, the sample cannot be considered as following a Gaussian (normal) distribution. On the other hand, if W > W<sub>crit</sub>, the sample does follow a Gaussian distribution, and the risk of error is determined by W<sub>crit</sub>. Thus, if one chooses a risk of error of 5%, W<sub>crit</sub> will be equal to 0.781, and for a risk of 1%, W<sub>crit</sub> will be equal to 0.842.

The first step of this test is to order the experimental measurements:

$$y_1 \leq y_2 \leq \dots \leq y_{n-1} \leq y_n$$

Number W is defined using formula (3).

$$W = \frac{1}{T_n} \left( \sum_{j=1}^p a_j d_j \right)^2 \quad (3)$$

where  $T_n = \sum_{i=1}^n (y_i - \bar{y})^2$ ;  $\bar{y}$  is the average of the

measurements ( $\bar{y} = \frac{1}{n} \sum_{i=1}^n y_i$ ); p is equal to  $\frac{n}{2}$  if n is

even and to  $\frac{n-1}{2}$  if  $n$  is odd; the  $a_j$  numbers are given by the Shapiro-Wilk table (Shapiro, 1965): for  $n = 10$ ,  $a_1 = 0.5739$ ;  $a_2 = 0.3291$ ;  $a_3 = 0.2141$ ;  $a_4 = 0.1224$ ;  $a_5 = 0.0399$ , and the  $d_j$  numbers are defined as  $d_j = y_{n-(j-1)} - y_j$ .

For each video, a sample of ten droplets was studied ( $n = 10$ ). The use of the Shapiro-Wilk test showed that for every sample, the  $W$  value (either for the ellipsoid axes or the apparent surface) was higher than  $W_{crit}$  (0.781 for a 5% risk, or 0.842 for a 1% risk, see Shapiro et al., 1965), which meant that every sample followed a Gaussian distribution. This demonstrated that the analysis of ten droplets was sufficient to determine the apparent dimensions of a droplet population. Thus, to study the dissolution rate of a chemical, ten droplets were taken into account at two depths, and to calculate the dimensions of each of these droplets, ten stills were analyzed over a homogeneous 10-cm path.

#### Calculation of the mean volume of a normal droplet population

When the normality of a sample (population:  $n$ ; standard deviation:  $\sigma$ ) is checked, the mean volume ( $\mu$ ) of a droplet sample can be calculated for a given chemical compound, injection flow and camera position. It can be said, with a probability given by Student-Fischer's parameter  $t$ , that the mean volume  $\mu$  is between  $\mu_0 - \lambda$  and  $\mu_0 + \lambda$ ,  $\mu_0$  and  $\lambda$  being defined by formulae (4) and (5), respectively.

$$\mu_0 = \frac{\sum_{j=1}^n x_j}{n} \quad (4)$$

$$\lambda = \frac{t \times \sigma}{\sqrt{n-1}} \quad (5)$$

In these formulae,  $x_j$  is the volume of droplet  $j$ , and  $n-1$  is the number of degrees of freedom. Accepting 1% risk of error led to  $t = 3.25$ , according to Student - Fischer's table.

### **3.2 Speed and initial volume of droplets vs solubility**

#### Speed of droplets

Figure 4 shows various chemical droplet speeds: most chemicals less dense than seawater have a specific mass close to  $0.8 \text{ g cm}^{-3}$  (except ethenyl acetate ( $\rho_{18^\circ\text{C}} = 0.93 \text{ g cm}^{-3}$ ) and 2-methoxy-2-methyl-propane ( $0.74 \text{ g cm}^{-3}$ )). Actually, the droplet speed varied with the nature of the chemicals and the initial volume of the droplets. The unique isolated point represents the speed of ethenyl acetate droplets. Its relatively low speed can be explained by its specific mass ( $\rho_{18^\circ\text{C}} = 0.93 \text{ g cm}^{-3}$ ) relatively close to that of seawater ( $\rho_{18^\circ\text{C}} = 1.02 \text{ g cm}^{-3}$ ).

#### Droplet initial volume vs solubility

Figure 5 represents the volume of droplets estimated from image treatment, at  $P_{+15}$  for chemicals less dense than seawater and at  $P_{-15}$  for 1,2-dichloroethane, showing that the droplet size varied with the solubility. This can be explained by the rapid dissolution of the chemi-

cals just after their injection into the column. Moreover, it can be noticed that a plume characteristic of instantaneous dissolution was observed during the 2-butanone dissolution experiment.

### **3.3 Dissolution rate**

Validation of the method. Validation of the experimental procedure needed also considering chemicals of different enough solubility and density values. For this reason, we first used 1,2-dichloroethane and 2-butanone. The dissolution rate of chemicals was determined by comparison of the droplet volumes at  $P_{\pm 15}$  and  $P_{\pm h}$  locations.

1,2-Dichloroethane has a low solubility ( $8.7 \text{ g L}^{-1}$  in pure water) and is denser than seawater ( $\rho_{18^\circ\text{C}} = 1.26 \text{ g cm}^{-3}$ , as compared to seawater :  $\rho_{18^\circ\text{C}} = 1.02 \text{ g cm}^{-3}$ ). On the contrary, 2-butanone has a high solubility ( $290 \text{ g L}^{-1}$ ) and is less dense than seawater ( $\rho_{18^\circ\text{C}} = 0.80 \text{ g cm}^{-3}$ ). In that respect, these chemicals have opposite characteristics. For both chemicals, the volume loss of a droplet was measured from one position to another (Table 5).

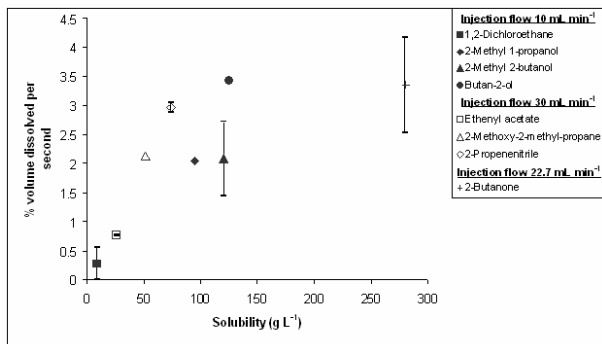
**Table 5. Volume variations of the 1,2-dichloroethane and 2-butanone droplets.**

Chemical	1,2-Dichloroethane	2-Butanone	
Injection flow ( $\text{mL min}^{-1}$ )	7.9	10.1	22.7
Volume variation of a droplet from $P_{-15}$ to $P_{-270}$ ( $\text{mm}^3$ )	0.2	4.3	
Volume variation of a droplet from $P_{+15}$ to $P_{+160}$ ( $\text{mm}^3$ )			2.8
Uncertainties ( $\text{mm}^3$ )	11.4	11.9	0.6

The volume variations of 1,2-dichloroethane droplets from  $P_{-15}$  to  $P_{-270}$  were lower than the estimated uncertainties. However, in case of emergency, it will be possible to estimate the volume of chemical which will dissolve in the water column, and consequently, the volume of chemical which will form slick(s) at sea surface or on seabed and then possibly drift in two dimensions.

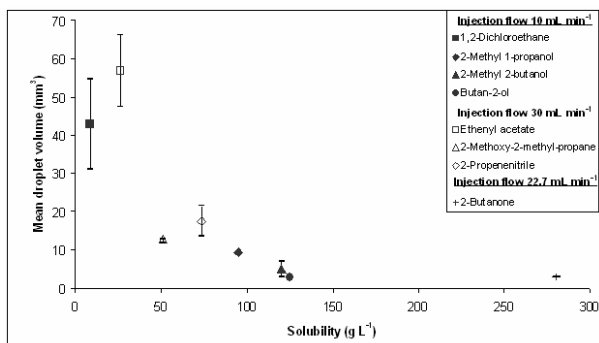
In the case of 2-butanone, on the opposite, a significant transfer was quantified during its upward flow.

It is worth noting, however, that the optimal injection flow of 2-butanone was difficult to define because of the high solubility of this compound ( $290 \text{ g L}^{-1}$ ). The injected droplets were polydispersed and an organic plume was observed near the outflow. Chemicals with high solubility will be difficult to study by the method described here, but responders will be informed about the possible formation of toxic cloud and, the necessity of taking into account the whole contaminated volume.

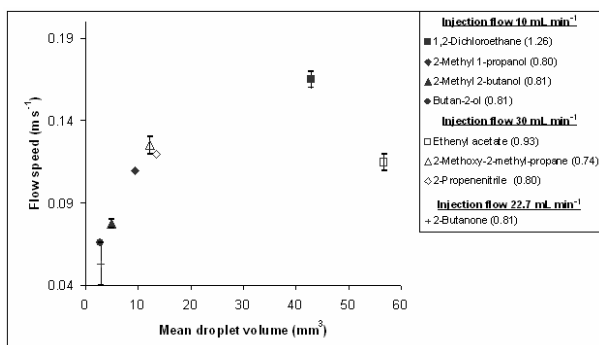


**Fig. 4. Dissolution kinetics of chemicals according to their solubility limit.** Black (full) marks are for chemicals injected at  $10 \text{ mL min}^{-1}$ ; white (empty) marks are for chemicals injected at  $30 \text{ mL min}^{-1}$ ; butan-2-one (cross) was injected at  $22.7 \text{ mL min}^{-1}$ .

As a matter of fact, in case of a wreck with a leaking tank, low solubility will lead to long-time duration of the spill at the sea surface or on the sea bed, while high solubility will have a shortening effect on this duration. Both cases may be considered as limiting ones.



**Fig. 5. Mean initial volume of droplets measured at  $P_{+15}$  or at  $P_{-15}$  according to their solubility.** Black (full) marks are for chemicals injected at  $10 \text{ mL min}^{-1}$ ; white (empty) marks are for chemicals injected at  $30 \text{ mL min}^{-1}$ ; butan-2-one (cross) was injected at  $22.7 \text{ mL min}^{-1}$ .



**Fig. 6. Flow speed of various chemicals according to the mean initial volume of their droplets.** The numbers between brackets following the names of the chemical substances are the densities of those substances. Black (full) marks are for chemicals injected at  $10 \text{ mL min}^{-1}$ ; white (empty) marks are for chemicals injected at  $30 \text{ mL min}^{-1}$ ; butan-2-one (cross) was injected at  $22.7 \text{ mL min}^{-1}$ .

## Other chemicals

Six other chemicals were studied. Figure 6 shows the results of these experiments. Black (full) and white (empty) points represent the case of injection flows of  $10 \text{ mL min}^{-1}$  and  $30 \text{ mL min}^{-1}$ , respectively. For 2-butanone, the injection flow was  $22.7 \text{ mL min}^{-1}$ . Analyzing distinctly both data sets (black and white points) confirmed that the dissolved volume percentage per second (determined by image treatment) increased, as expected, with the solubility.

The dissolution rate can be expressed as a volume loss during a flow time or between two depths. However, the dissolution rate of a chemical droplet varies according to the initial conditions. Table 6 summarizes the results found for the eight chemicals tested. It can be seen that the volume loss varied with several factors, namely: the initial injection flow, the droplet size (volume and surface area), the droplet speed and the distance between the two depths used for analysis. It can be noticed that the length between two depths is not always the same, varying from 145 to 255 cm. This is due to the fact that the chemicals did not exhibit the same solubility, the maximum length between two depths occurring for the less soluble substances.

**Table 6. Dissolution kinetics for 8 chemicals.** The droplet volume at  $P_{-15}$  or  $P_{+15}$  was calculated after image treatment. I: injection flow; D: distance between the location of measurements;  $\Delta V$ : loss of volume.

Chemicals	I ( $\text{mL min}^{-1}$ )	D (cm)	$\Delta V$ (%)
1,2-Dichloroethane	7.9	255	0.0
	10.1	255	6.9
Ethenyl acetate	30.0	250	17.5
	32.5	250	15.9
2-Methoxy-2-methyl-propane	32.0	250	42.7
	34.0	250	42.6
2-Propenenitrile	29.5	250	59.6
	32.0	250	63.4
2-Methyl 1-propanol	10.0	250	46.3
2-Methyl 2-butanol	6.6	210	52.2
	7.5	210	71.4
Butan-2-ol	7.0	150	100.0
2-Butanone	22.7	145	9.3

## 4. Conclusion

The method described in this paper aimed at giving a rapid assessment of the dissolution rate of chemicals in seawater. It could be particularly useful in case of wreckage of a tanker or accidental release of chemicals at sea.

For that purpose, a unique five-meter high column was built at the *Cedre* in Brest, France. Chemicals can be introduced at the bottom or at the top of the column,

depending on the density of the product which is supposed to move along the column as separate droplets.

Recording droplet flow by use of a digital video camera, it was shown that the apparent dimensions of a reduced set of droplets i) followed a Gaussian distribution, ii) gave a way to determine the volume variation of droplets along the column iii) was able to characterize the dissolution rate of various substances.

The first results were in accordance with what was expected for the dissolution rate, that is, the more soluble the product, the higher the volume loss, and the smaller the droplets. But this trend was not always observed, due to some limitations which mainly depended on the solubility of the chemicals in water and, maybe, on interface properties in the system seawater / chemical. This point calls for particular studies. The C.E.C. was checked to be efficient for solubilities in the range 8 (1,2-dichloroethane) to 125 g L<sup>-1</sup> (2-butanol).

It can also be a mean to take into account the change of scale between laboratory experiments and environmental situations. As a matter of fact, for field action, the correlations determined by the C.E.C. and the resulting curves will be very helpful for predicting the behaviour of either a substance leaking from a wreck, which would be liable to form a toxic cloud on the sea surface, or a substance released from a leaking ship on the sea surface, which could form toxic layers on the sea-floor, and thus be detrimental to the local fauna and flora.

The experimental uncertainties have to be considered with respect to the application domain: a massive pollution alert. In that respect, the C.E.C. will be a valuable tool, since indications about the behaviour of the chemical product, and hence advices for the definition of response techniques could be available in less than three days.

Some column modifications are currently under development in order to study either more soluble or hardly soluble substances.

## 5. Acknowledgements

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