# Operational Device and Procedure to Test the Initial Dissolution Rate of Chemicals After Ship Accidents: the *Cedre* Experimental Column

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**Abstract:** This paper describes an experimental procedure recently developed to simulate and study the behaviour of various chemicals in seawater during their transfer in a 5 m deep water column. Since chemical pollution can be harmful to the environment, anticipating the evolution of a chemical spill is important for authorities, so that they can act rapidly and efficiently after a spill. In the case of a sunken wreck containing chemicals with a lower density than seawater in its leaking tanks, it could be useful to estimate the quantity of chemicals that should be found at the sea surface. On the other hand, in the case of a spill occurring at the sea surface, the mass of chemicals liable to sink and accumulate on the seabed without being dissolved during sinking is an important piece of information required to choose the most suitable response strategy.

The solubility of a particular chemical is not always available from the literature. In particular, the solubility in seawater is seldom documented and, whenever it is, it is usually in the form of solubility limits. As important as this parameter may be, it is not the most significant one in situations in which the interface between the (sea) water and the chemical involved undergoes permanent renewal. A more operational parameter would be the initial dissolution rate.

The *Cedre* Experimental Column (C.E.C.) was designed for this purpose and a method was defined. The volume and dimensions of droplets of chemicals were studied in order to characterize the dissolution of different products throughout their journey through the water column. The dissolution rate can be expressed as a volume loss during a flow time or between two given depths. Experiments were performed on eight chemicals with different water solubility limits (8.7 to 290 g $L^{-1}$) using video imagery to analyze the chemicals' behaviour. If the initial dissolution rate is dependent on solubility, it appears clearly that other physical parameters are also relevant to predict the behaviour of a product, for instance its density and viscosity. In addition to these intrinsic parameters, the dissolution kinetics of a product are also linked to its injection flow in the water column, determined, for example, by the size of the hole in the ship which will define the droplet speed.

The C.E.C is therefore an operational tool which can be used to study the behaviour of specific chemicals, either as part of a particular study or in the event of a spill, taking into account all the relevant factors involved. It provides accurate and detailed information on the product's dissolution kinetics, enabling it to be used to assist in decision-making for emergency response.

## INTRODUCTION

One of the consequences of the increasing global economy is the continuous development of international maritime transport. For instance, from 1970 to 1995, the maritime transportation of chemicals sharply increased by 270% [1]. In the English Channel, shipping traffic increased from 30 million tonnes in 1989 to 150 million tonnes in 2000 [2]. One of the downsides of this intensifying traffic was the occurrence of numerous accidents, such as the sinking of the *Ievoli Sun* on October 31st, 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 waters [3]. 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 the event of release, 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 [4]. This incident and others, at sea [5] or in fresh waters (e.g. benzene spill in Song Hua River, China, 2005; [6, 4, 7]), 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 a spill.

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 effort, a key point was to estimate the quantity of styrene that could be

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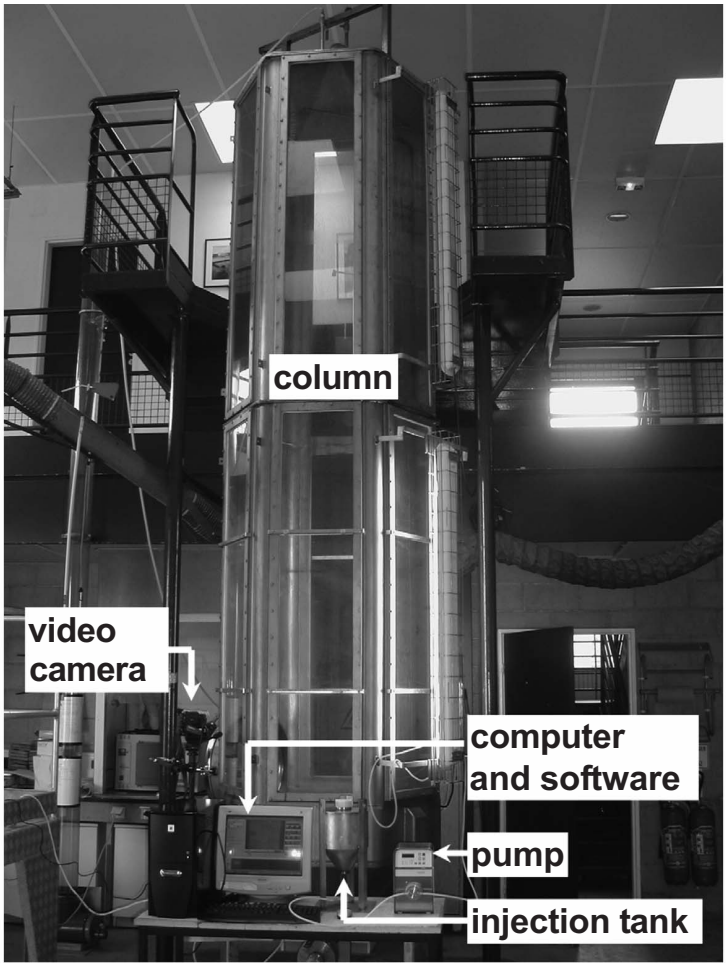


**Fig. (1).** The *Cedre* Experimental Column (C.E.C.) and its tools.

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.

As an organization specialized in operations in case of accidental water pollution, *Cedre* (*Ce*ntre of *D*ocumentation, *R*esearch and *E*xperimentation 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. Chemicals can be introduced at the bottom or at the top of the column, depending on the density of the product which is expected to move along the column as separate droplets. A method using this equipment was developed to give a rapid assessment of the dissolution rate of chemicals in seawater, information which is particularly useful in case of wreckage of a tanker or a chemical spill at sea.

The dissolution rate of chemicals 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 [8]. To control the initial conditions, the chemical behaviour was studied by observing droplet flows. The method consisted of determining the variation in volume of droplets between two depths, using a video acquisition and processing system.

If an isolated droplet is spherical, it will be distorted to an ellipsoidal shape when subjected to different forces, such as gravity and interfacial forces [9]. Models of droplet behaviour have been established, based on the assumption of such a shape [10]. 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 [8], but droplets can also be broken when the kinetic energy exceeds the surface energy [11, 12].

All these phenomena must be taken into account to analyze the droplet flow and behaviour. The aim of the subject is to obtain the dissolution rate by droplet characterization.

## EXPERIMENTATION

### Experimental Setup

The equipment is composed of the *Cedre* Experimental Column (C.E.C.) equipped with an injection system and a video system.

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

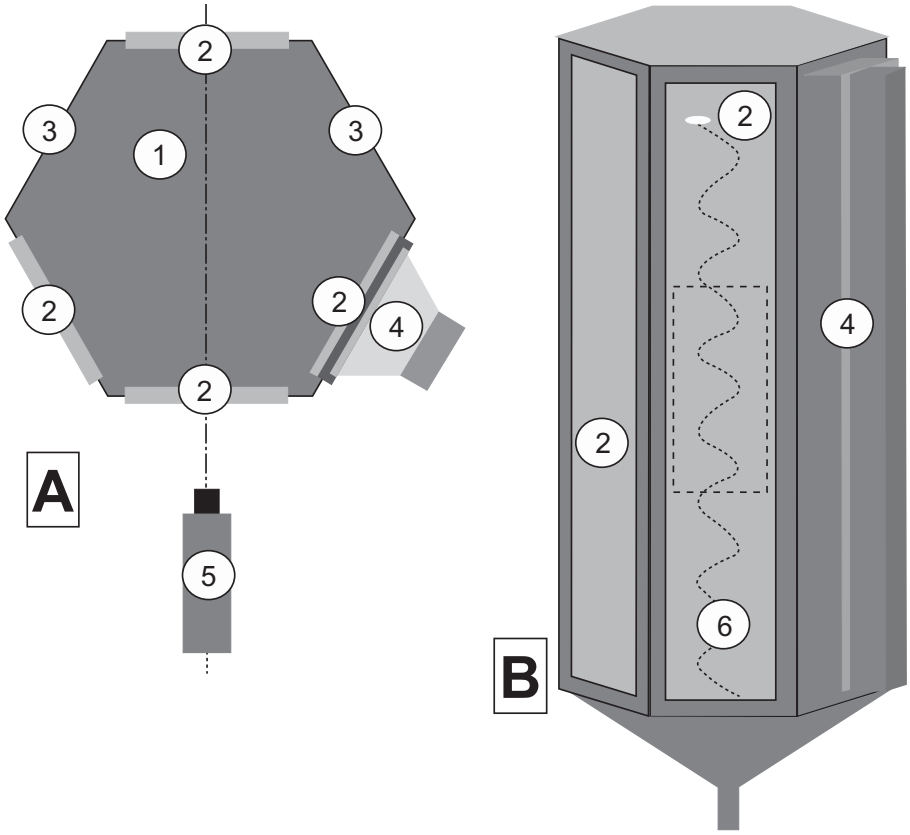


**Fig. (2).** Diagram of the *Cedre* Experimental Column (C.E.C.). Horizontal section (**A**) of the column with the camera position, outside of the column, with droplet movement. 1. Seawater inside the column; 2. Glass sides; 3. Opaque sides; 4. Cold white lights; 5. Digital video camera on tripod;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

both better resistance than a parallelepiped and better optical properties for video observation than a cylinder. Opposite sides are 0.8 meters apart, giving 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 undissolved 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 the 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 the bottom of the column to inject chemicals, depending on their specific mass (higher or lower than that of seawater). A stainless steel tank was used to stock chemicals prior to their injection into the column. A pressure valve was placed on top of the column to prevent any depressurization due to pumping. A gear pump (*ISMATEC* –IP 65 MCP-Z Process, Labortechnik-Analytik, Glattburgg-Zürich) coupled with a pump head (*Micropump* GA-T23, Labortechnik-Analytik, Glattburgg-Zürich) was used to inject the chemicals along the vertical axis in the middle of the column, with a regular and well-defined flow (working range: 6-35 mL $min^{-1}$) by use of a 40-cm long injection tube. A 2-mm wide aperture was used throughout the present study.

Droplet positions were noted as $P_0$ for injection depth, and $P_{\pm h}$ for a droplet located h centimetres above (+ sign) or below (- sign) $P_0$. 2.5 L of chemical were injected, so that the product concentrations in seawater remained below the solubility limit – apart from styrene.

A video camera (Sony-DCR-TRV8), with Videostudio 7 (software distributed by Ulead) was used to capture and register all videos of droplet flows. Virtual dub (distributed by Avery Lee) was used to deinterlace every video while Aviméca (distributed by Microsoft) was used to determine the apparent lengths of the major and minor axes of the ellipsoidal droplets at each still in video sequences.

## Products

The seawater (salinity 27 kg $m^{-3}$) was pumped from Brest harbour, filtered on sand to take out suspended particles with a size of more than 25 µm and UV-treated (25 mj/$cm^2$) before use. The aim of this treatment is to prevent flocculation between chemical compounds and suspended matter which could reduce the dissolution kinetics of compounds in seawater. The mean water temperature during the experiments was 18 °C.

**Table 1. Mass Density, Solubility and Viscosity of the Studied Chemicals**

| CAS Number | Chemical IUPAC Name | Provider | Purity | Mass Density at 18 °C ($g\ cm^{-3}$) | Solubility in Pure Water at 20 °C ($g\ L^{-1}$) | Viscosity at 18 °C (mPa s) |
|---|---|---|---|---|---|---|
| 100-42-5 | Styrene * | *ATOFINA* | - | 0.91 | 0.3 | 0.75 |
| 107-06-2 | 1,2-Dichloroethane * | *ATOFINA* | - | 1.26 | 8.7 | 0.84 |
| 108-05-4 | Ethenyl acetate ** | *ACROS ORGANICS* | 99% | 0.93 | 23 | 0.43 |
| 1634-04-4 | 2-Methoxy-2-methyl-propane ** | *ACROS ORGANICS* | 99% | 0.74 | 51 | 0.36 |
| 107-13-1 | 2-Propenenitrile ** | *ACROS ORGANICS* | 99% | 0.81 | 73.5 | 0.35 |
| 111-69-3 | Hexane dinitrile ** | *ACROS ORGANICS* | 99% | 0.96 | 90 | 6.66 |
| 78-83-1 | 2-Methyl 1-propanol** | *ACROS ORGANICS* | 99% | 0.80 | 95 | 4.09 |
| 75-85-4 | 2-Methyl 2-butanol** | *ACROS ORGANICS* | 99% | 0.81 | 120 | 5.19 |
| 78-92-2 | Butan-2-ol ** | *ACROS ORGANICS* | 99% | 0.81 | 125 | 4.40 |
| 111-55-7 | 2-Acetyloxyethyl acetate** | *ACROS ORGANICS* | 97% | 1.11 | 160 | 2.97 |
| 78-93-3 | 2-Butanone * | *SDS* | 99% | 0.81 | 290 | 0.43 |

*Sources:* * *INRS Institut National de Recherche et de Sécurité – French National Institute for Research and Security.*
** *ACROS ORGANICS.*

The chemicals studied in this project and some of their physicochemical parameters are listed in Table **1**. The solubility of the chemical products selected ranges from 8.7 to 290 g $L^{-1}$. This provides a good idea of the dissolution and the behaviour of droplets in seawater.

## Video Camera Setup

### Camera Positioning

The video 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. The test pattern, graduated in centimetres, was placed along the vertical axis inside the column, directly below the seawater surface so that the "zero" of the test pattern corresponded to the surface level. It pictured a 10 cm × 10 cm field within which the droplet dimensions were measured, assuming that the droplet volume did not change during this 10-cm path.

Droplets were formed near the injection aperture. However, in this zone, the shape variations were considerable. 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. This distance increased up to 2.5 m for the least soluble compounds.

### Video Acquisition

After injection of the chemical, a 30 second video of the droplet flow was filmed at each previously defined depth, at a rate of 25 frames per second.

### Video Treatment

For analysis, every film was cut into separate 720 × 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 [13]. So, the "camera-to-droplet distance" varied slightly and droplets sometimes moved away from the focal plane. Therefore, the blurriest images had to be eliminated before further analysis to obtain coherent results.

After software calibration with the video test pattern, 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. Therefore, the apparent surface ($S_a$) of the droplets could be calculated using formula (1):

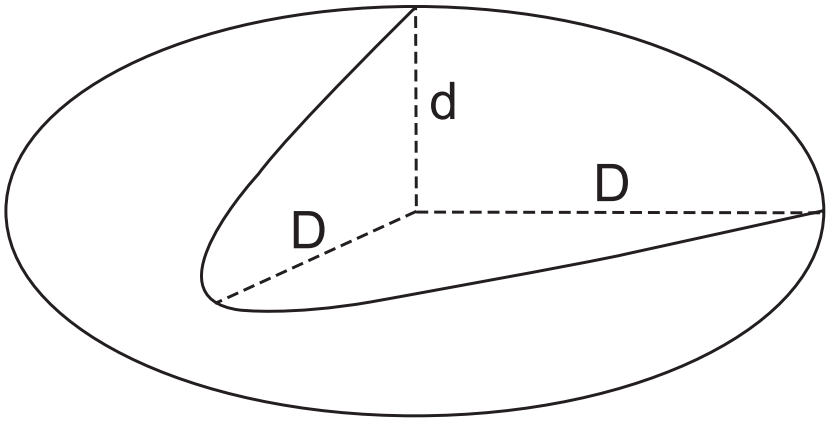


**Fig. (3).** Oblate ellipsoid parameters: minor (**d**) and major (**D**) axes.

**Table 2. Optimal Injection Flow for Each Chemical**

| Chemical | Optimal Injection Flow (mL $min^{-1}$) |
|---|---|
| Styrene | 6.5 |
| 1,2-Dichloroethane | 10.1 |
| Ethenyl acetate | 30.0 |
| 2-Methoxy-2-methyl-propane | 32.0 |
| 2-Propenenitrile | 29.5 |
| Hexane dinitrile | 10.1 |
| 2-Methyl 1-propanol | 10.0 |
| 2-Methyl 2-butanol | 6.6 |
| Butan-2-ol | 7.0 |
| 2-Butanone | 22.7 |

$$S_a = \frac{\partial \times d \times D}{4} \quad (1)$$

This parameter was 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 correct parameters.

Furthermore, the volume (V) and the actual surface (S) of the droplets were calculated using formulae (2) and (3):

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

$$S = \frac{\pi D}{2}\left(D + \frac{d}{2e} \times \ln\left(\frac{1+e}{1-e}\right)\right) \quad (3)$$

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 [14].

## EXPERIMENTAL PARAMETERS

### Optimal Injection Flow

The injected droplets must have similar sizes and be spaced out enough to limit interaction 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 interaction. This led to the determination of an optimal injection rate for every chemical (Table **2**). This optimal injection rate was determined taking into account the solubility limit of each product and this rate was obtained after 4 tests.

It is worth noting that the optimal injection flow of 2-butanone was difficult to define because of the high solubility of this compound (290 g $L^{-1}$). The injected droplets were polydispersed and an organic plume was observed near the outflow. This shows one of the limitations of the method: products whose solubility is higher than about 300 g $L^{-1}$ (the solubility of 2-butanone is 290 g $L^{-1}$) cannot be studied by the method described here.

### 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. This distance was selected due to the wide range of solubilities of tested compounds: droplets of the most soluble compound disappeared completely beyond 1.2 m.

### Mean Initial Droplet 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 droplets injected could be evaluated and compared with the volume 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 $min^{-1}$), giving the same results.

Given the low solubility of 1,2-dichloroethane in water (8.7 g $L^{-1}$), the droplet volume did not vary during the flow between $P_0$ and $P_{-15}$. So, the initial volume was calculated at $P_{-15}$ where the droplet shape was checked to be ellipsoidal.

Table **3** shows that the difference in droplet volume between the two methods was lower than the uncertainties for the values calculated from image treatment (to the order of

**Table 3. Initial Volume of 1,2-dichloroethane Droplets Estimated Using $M_1$ and $M_2$**

| Injection Flow (mL min$^{-1}$) | Number of Droplets Injected Per Min | Mean Volume of 1,2-dichloroethane Droplets (mm$^3$) | |
|---|---|---|---|
| | | Counting at $P_0$ | Image Treatment at $P_{-15}$ |
| 7.9 | 134 | 58.7 | 54.7 ± 4.3 |
| 10.1 | 162 | 62.3 | 61.9 ± 3.1 |

**Table 4. Comparison of the Apparent Dimensions of One Droplet, Calculated Considering 10 or 40 Stills**

| | d (mm) | D (mm) | $S_a$ (mm$^2$) |
|---|---|---|---|
| $I_{40}$ (n=40) | **9.5** | **13.7** | **102.2** |
| $I_{10}$ (n=10) | **9.7** | **13.5** | **102.8** |
| Variations | **2 %** | **1.5 %** | **0.5 %** |

$10^{-5}$). Thus, the assumption made about droplet shape was satisfactory, and droplets could be assimilated to ellipsoids.

## RESULTS AND DISCUSSION

### Determination of the Minimum Number of Stills and Droplets to Analyze in Order to Obtain Statistically Correct Results

The mean droplet dimensions were calculated in two stages. First, the apparent dimensions of droplets of chemical were calculated using stills from the video imagery. It was therefore necessary to determine the number of droplets and stills which needed to be analyzed to give statistically correct results. Then, the homogeneity of these measurements was checked using the Shapiro-Wilk test [14] 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 $P_{+15}$, for an injection flow of 6.5 mL min$^{-1}$. The mean apparent lengths of the axes (D, d) were measured, considering ten ($I_{10}$) and forty ($I_{40}$) stills. Table **4** shows that there exists hardly any discrepancy between $I_{10}$ and $I_{40}$. Therefore, throughout the 10-cm droplet flow, only ten stills needed to be analyzed to determine the mean apparent dimensions of one droplet.

### 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 [14]. It involves calculating a value W and comparing it to a critical value $W_{crit}$. If $W < W_{crit}$, the sample cannot be considered as following a Gaussian (normal) distribution. On the other hand, if $W > W_{crit}$, the sample does follow a Gaussian distribution, and the risk of error is determined by $W_{crit}$. Thus, if one chooses a risk of error of 5%, $W_{crit}$ will be equal to 0.781, and for a risk of 1%, $W_{crit}$ will be equal to 0.842.

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

$$y_1 \le y_2 \le \ldots \le y_{n-1} \le y_n$$

Value W is defined using formula (4).

$$W = \frac{1}{T_n}\left(\sum_{j=1}^{p} a_j d_j\right)^2, \quad (4)$$

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 *et al.*, 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 $d_j$ values 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 [14]), which meant that every sample followed a Gaussian distribution (Table **5**). 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 considered 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: σ) is checked, the mean volume (μ) 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 μ is between $\mu_0 - \lambda$ and $\mu_0 + \lambda$, $\mu_0$ and $\lambda$ being defined by formulae (5) and (6), respectively.

$$\mu_0 = \frac{\sum_{j=1}^{n} x_j}{n} \quad (5)$$

$$\lambda = \frac{t \times \sigma}{\sqrt{n-1}} \quad (6)$$

**Table 5. Shapiro-Wilk's W Values Calculated for the Apparent Surface ($S_a$), and the Minor (d) and Major (D) Axes with 10 Droplets For Each Chemical Under Study. The Risk Taken by Accepting the Hypothesis of Normal Distribution is Also Given**

| Chemical Product | Injection Flow (mL min$^{-1}$) | Position | W ($S_a$) | Risk (%) | W (D) | Risk (%) | W (d) | Risk (%) |
|---|---|---|---|---|---|---|---|---|
| 1,2-Dichloroethane | 10 | Low | 0.946 | <1 | 0.916 | <1 | 0.790 | <5 |
| | | High | 0.921 | <1 | 0.820 | <5 | 0.958 | <1 |
| Ethenyl acetate | 30 | Low | 0.939 | <1 | 0.926 | <1 | 0.928 | <1 |
| | | High | 0.879 | <1 | 0.945 | <1 | 0.914 | <1 |
| 2-Methoxy-2-methyl-propane | 32 | Low | 0.973 | <1 | 0.939 | <1 | 0.949 | <1 |
| | | High | 0.894 | <1 | 0.920 | <1 | 0.976 | <1 |
| 2-Propenenitrile | 29.5 | Low | 0.874 | <1 | 0.859 | <1 | 0.960 | <1 |
| | | High | 0.917 | <1 | 0.923 | <1 | 0.959 | <1 |
| 2-Methyl 1-propanol | 10 | Low | 0.956 | <1 | 0.975 | <1 | 0.936 | <1 |
| | | High | 0.912 | <1 | 0.930 | <1 | 0.969 | <1 |
| 2-Methyl 2-butanol | 6.61 | Low | 0.866 | <1 | 0.941 | <1 | 0.989 | <1 |
| | | High | 0.908 | <1 | 0.905 | <1 | 0.915 | <1 |
| | 7.45 | High | 0.897 | <1 | 0.900 | <1 | 0.939 | <1 |
| Butan-2-ol | 7 | Low | 0.864 | <1 | 0.929 | <1 | 0.961 | <1 |
| | | High | 0.884 | <1 | 0.833 | <5 | 0.908 | <1 |
| 2-Butanone | 22.7 | Low | 0.950 | <1 | 0.897 | <1 | 0.941 | <1 |
| | | Middle | 0.956 | <1 | 0.951 | <1 | 0.965 | <1 |

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.

### *Speed of Droplets*

Fig. (**4**) shows various chemical droplet speeds. Most chemicals less dense than seawater have a specific mass close to 0.8 g cm$^{-3}$ (except ethenyl acetate ($\rho_{18\,°C}$ = 0.93 g cm$^{-3}$) and 2-methoxy-2-methyl-propane (0.74 g cm$^{-3}$)). In reality, the droplet speed varied with the nature of the chemicals (density, viscosity and solubility) 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 ($\rho_{18\,°C}$ = 0.93 g cm$^{-3}$), which is relatively close to that of seawater ($\rho_{18\,°C}$ = 1.02 g cm$^{-3}$).

### *Initial Droplet Volume vs. Solubility*

Fig. (**5**) represents the volume of droplets estimated from image treatment, at $P_{+15}$ for chemicals less dense than sea-

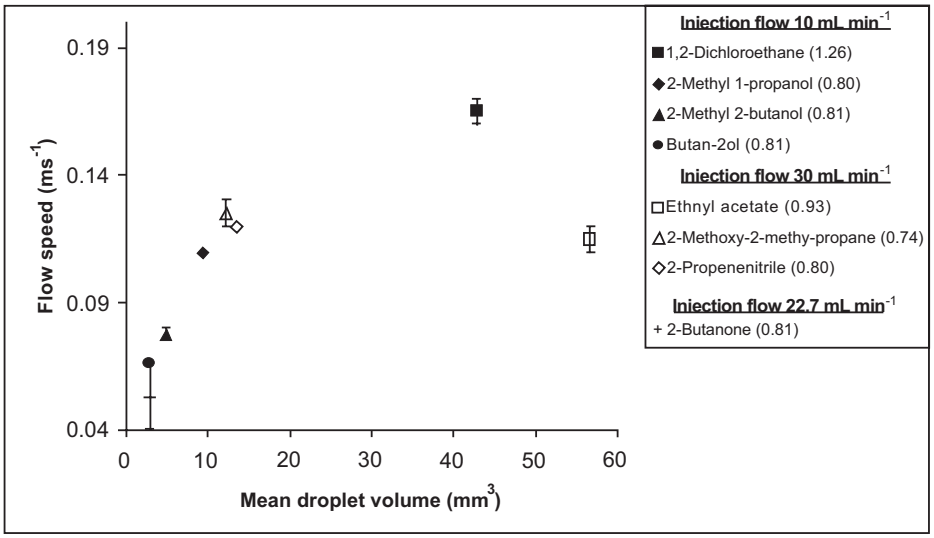


**Fig. (4).** Flow speed of various chemicals according to the mean initial volume of their droplets. The numbers in brackets following the names of the chemical substances are the densities of those substances. Black (full) marks are for chemicals injected at 10 mL min$^{-1}$; white (empty) marks are for chemicals injected at 30 mL min$^{-1}$; 2-butanone (cross) was injected at 22.7 mL min$^{-1}$.

**Table 6. Volume Variations of the 1,2-dichloroethane and 2-butanone Droplets**

| | Chemicals and Injection Flow (mL $min^{-1}$) | | |
|---|---|---|---|
| | 1,2-Dichloroethane | | 2-Butanone |
| | Injection Flow: 7.9 | Injection Flow: 10.1 | Injection Flow: 22.7 |
| Volume variation of a droplet from $P_{-15}$ to $P_{-270}$ ($mm^3$) | 0.2 | 4.3 | |
| Volume variation of a droplet from $P_{+15}$ to $P_{+160}$ ($mm^3$) | | | 2.8 |
| Uncertainty ($mm^3$) | 11.4 | 11.9 | 0.6 |

tion rate of the chemicals was determined by the comparison of the droplet volumes at $P_{\pm 15}$ and $P_{\pm h}$ locations.

1,2-Dichloroethane has a low solubility (8.7 g $L^{-1}$ in pure water) and is denser than seawater ($\rho_{18\,°C}$ = 1.26 g $cm^{-3}$, as compared to seawater: $\rho_{18\,°C}$ = 1.02 g $cm^{-3}$). On the contrary, 2-butanone has a high solubility (290 g $L^{-1}$) and is less dense than seawater ($\rho_{18\,°C}$ = 0.80 g $cm^{-3}$). In this respect, these chemicals have opposite characteristics. For both chemicals, the volume loss of a droplet from one position to another was measured (Table **6**). The volume variations of 1,2-dicholoroethane droplets from $P_{-15}$ to $P_{-270}$ were lower than the estimated uncertainties. This result shows a second limitation of the method. The dissolution rate of compounds of solubility lower than 8.7 g $L^{-1}$ cannot be determined by this method. On the other hand, for 2-butanone, a significant transfer was quantified during the upward flow.

### Other Chemicals

Six other chemicals, selected due to their solubility limits, were studied. Fig. (**6**) shows the results of these experi-

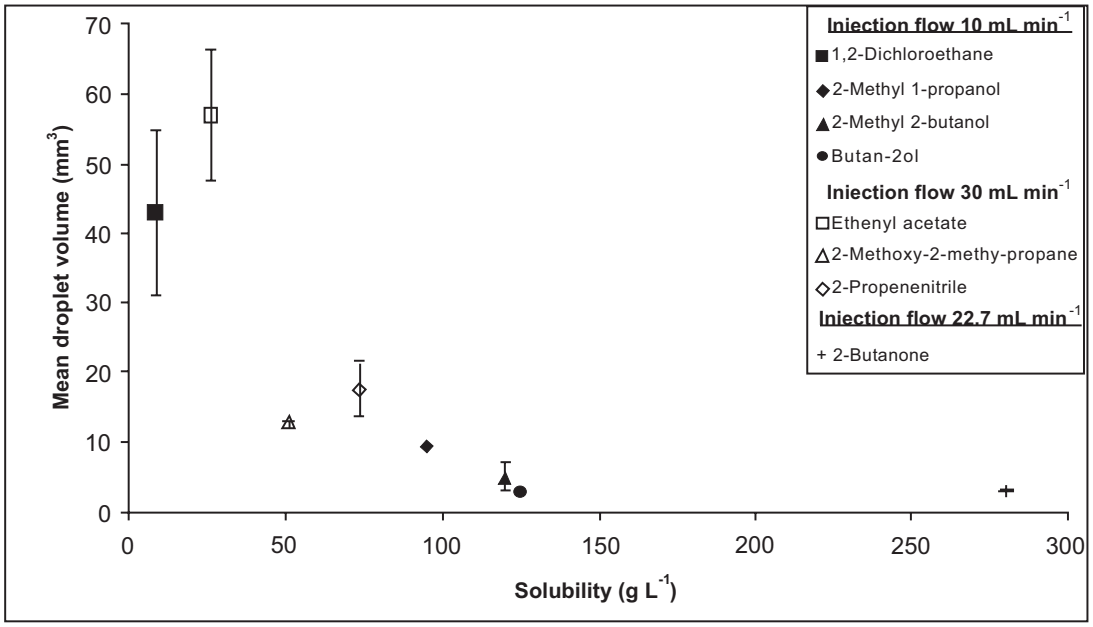


**Fig. (5).** Mean initial volume of droplets measured at $P_{+15}$ or at $P_{-15}$ according to their solubility. Black (full) marks are for chemicals injected at 10 mL $min^{-1}$; white (empty) marks are for chemicals injected at 30 mL $min^{-1}$; 2-butanone (cross) was injected at 22.7 mL $min^{-1}$.

water 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 chemicals just after their injection into the column. Moreover, it can be noted that a plume characteristic of instantaneous dissolution was observed during the 2-butanone dissolution experiment. For the same injection rate, the most soluble products show the smallest droplet size.

### *Dissolution Rate*

### Methodology Validation

The validation of the experimetal procedure also required the consideration of chemicals with solubility and density values which were significantly different. For this reason, we first used 1,2-dichloroethane and 2-butanone. The dissolu-

ments. Black (full) and white (empty) dots represent the case of injection flows of 10 mL $min^{-1}$ and 30 mL $min^{-1}$, respectively. For 2-butanone, the injection flow was 22.7 mL $min^{-1}$. Analyzing both data sets distinctly (black and white dots) 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 **7** 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.

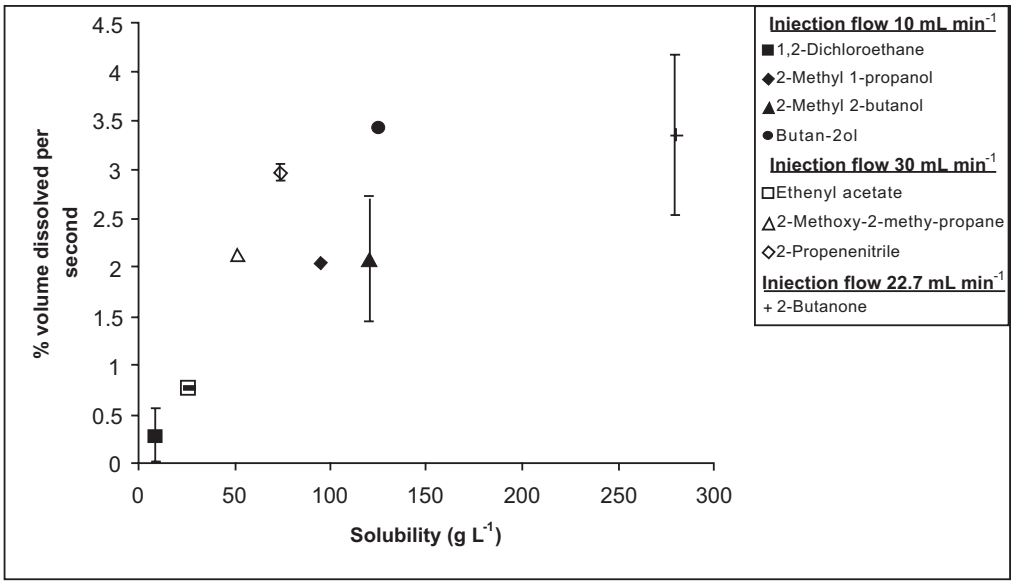


**Fig. (6).** Dissolution rate of chemicals according to their solubility, assuming that the dissolution rate along the column is constant. Black (full) marks are for chemicals injected at 10 mL $min^{-1}$; white (empty) marks are for chemicals injected at 30 mL $min^{-1}$; 2-butanone (cross) was injected at 22.7 mL $min^{-1}$.

**Table 7. Dissolution Kinetics for 8 Chemicals. The Droplet Volume at P-15 or P+15 was Calculated After Image Treatment**

| Chemicals | Injection Flow (mL $min^{-1}$) | Distance Between the 2 Depths (cm) | Flow Time Between the 2 Depths (s) | Droplet Area at $P_{+15}$ or $P_{-15}$ ($mm^2$) | Droplet Volume at $P_{-15}$ or $P_{+15}$ ($mm^3$) | Volume Loss Between the 2 Depths ($mm^3$) | Volume Loss Between the 2 Depths (%) |
|---|---|---|---|---|---|---|---|
| 1,2-Dichloroethane | 7.9 | 255 | 15.3 | 69.7 | 54.7 | 0.0 | 0.0 |
| | 10.1 | 255 | 14.4 | 75.9 | 61.9 | 4.3 | 6.9 |
| Ethenyl acetate | 30.0 | 250 | 22.7 | 82.9 | 66.1 | 11.6 | 17.5 |
| | 32.5 | 250 | 20.8 | 66.1 | 47.3 | 7.5 | 15.9 |
| 2-Methoxy-2-methyl-propane | 32.0 | 250 | 20.8 | 25.8 | 11.7 | 5.0 | 42.7 |
| | 34.0 | 250 | 19.2 | 27.1 | 12.9 | 5.5 | 42.6 |
| 2-Propenenitrile | 29.5 | 250 | 20.8 | 28.6 | 13.6 | 8.1 | 59.6 |
| | 32.0 | 250 | 20.8 | 39.2 | 21.6 | 13.7 | 63.4 |
| 2-Methyl 1-propanol | 10.0 | 250 | 22.7 | 22.9 | 9.5 | 4.4 | 46.3 |
| 2-Methyl 2-butanol | 6.6 | 210 | 28.0 | 10.4 | 2.3 | 1.2 | 52.2 |
| | 7.5 | 210 | 26.3 | 18.0 | 7.0 | 5.0 | 71.4 |
| Butan-2-ol | 7.0 | 150 | 22.7 | 10.3 | 2.2 | 2.2 | 100.0 |
| 2-Butanone | 22.7 | 145 | 22.0 | 10.4 | 3.0 | 2.8 | 9.3 |

The length between two given 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.

## CONCLUSIONS

The results of the experiments performed as part of this study underline the duality between the solubility limit of a compound and its solubility kinetics in case of a release at sea. Data concerning solubility limits is not enough in itself to predict the volume of a product which will dissolve in seawater during its transfer, for example, from the bottom to the sea surface.

Recording droplet flow by use of a digital video camera showed that the apparent dimensions of a reduced set of droplets i) followed a Gaussian distribution, ii) provided a way to determine the volume variation of droplets along the

column, iii) were 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. However, this trend was not always observed, due to certain limitations which mainly depended on the solubility of the chemicals in water. The experiments showed that other intrinsic and external parameters also affect the behaviour of chemicals in the water column. The C.E.C. was checked to be efficient for solubilities in the range of 8 (1,2-dichloroethane) to 125 g $L^{-1}$ (2-butanol). Some column modifications are currently under development in order to study either more soluble or hardly soluble substances.

In terms of field applications, the correlations determined by the C.E.C. and the resulting graphs will be very helpful for accurately 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 at the sea surface, which could form toxic layers on the sea-floor, and thus be detrimental to the local flora and fauna.

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

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## REFERENCES

[1] Le Floch S. Déversements accidentels de produits chimiques en mer: profils de danger et analyse d'accidents. In report Cedre n°S.2000.04, Published by Centre de Documentation, de recherche et d'Expérimentations sur les pollutions accidentelles des eaux (Cedre) 2000; pp. 53.

[2] Mamaca E, Cabioc'h F, Le Floch S. Drawing up a list of chemical compounds representing the highest risk for marine environment. Proceedings of the 4th European Meeting on Environmental Chemistry (EMEC4), Plymouth, England, 10-13 Dec 2003.

[3] Law RJ, Kelly C, Matthiessen P, Aldridge J. The loss of the chemical tanker *Ievoli Sun* in the English Channel, Oct 2000. Mar Pollut Bull 2003; 46: 254-7.

[4] UNEP. The Songhua River Spill, China, December 2006. In Field Mission Report. United Nations Environment Programme. 2006; p. 26.

[5] Le Floch S, Thomas A. Expertise de l'épave de l'ECE: Etude du comportement de l'acide phosphorique dans l'eau de mer. In report Cedre n° R.06.39.C/3116, Published by Centre de Documentation, de recherche et d'Expérimentations sur les pollutions accidentelles des eaux (Cedre) Sept 2006; p. 22.

[6] Calvez I, Kerambrun L, De Nanteuil E, Beau N. Explosion d'une usine pétrochimique, Jilin. In Lettre Technique Eaux Intérieures, Published by Centre de Documentation, de recherche et d'Expérimentations sur les pollutions accidentelles des eaux (Cedre) 2005; pp. 7-8, 15.

[7] Ambrose P. China involved in massive chemical spill. News/Mar Pollut Bull 2006; 52: 3-6.

[8] Giovannacci D. Contribution à l'étude des échanges à l'interface bulle liquide, issue d'un éjecteur venturi horizontal, en vue du traitement des poussières. Thèse. University Denis Diderot-Paris 7. 2002; p. 188.

[9] Danmoto Y, Fujiwara A, Hishida K, Maeda M. Bubble deformation and flow structure measured by double shadow images and PIV/LIF. Expfluids 2004; 36: 157-65.

[10] Wu Y, Zinchenko AZ, Davis RH. Ellipsoidal model for deformable drops and application to non-Newtonian emulsion flow. J Non-Newton Fluid 2002; 102: 281-98.

[11] Whyte DS, Davidson MR, Carnie S, Rudman MJ. Calculation of droplet deformation at intermediate Reynolds number using a volume of fluid technique. ANZIAM J 2000; 42E: C1520-53.

[12] Simon M, Smith SA, Bart HJ. The drop population balance model - Estimation of breakage and coalescence. Chem Eng Technol 2003; 26: 745-50.

[13] Ellingsen K, Risso F. On the rise of an ellipsoidal bubble in water: oscillatory paths and liquid-induced velocity. J Fluid Mech 2001; 440: 235-68.

[14] Shapiro SS, Wilk MB. An analysis of variance test for normality (complete samples). Biometrica 1965; 52: 591-611.

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