# REMOTE DETERMINATION OF RESIDUAL DE-ICER WITH AN OPTICAL SPECTROSCOPIC TOOL

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## ABSTRACT

Road winter maintenance is based on de-icers to avoid the presence of ice or the persistence of snow onto the pavement, and therefore maintain an appropriate grip level. The spreading takes place before the occurence of the slippery phenomenon, or once snow and/or ice already are present. The de-icer eases their melting at negative temperatures. Poor weather conditions, traffic, water flows at the surface induce de-icer losses that need to be known to properly appreciate the amount to add onto the road.

Residual de-icers measurements have shown limits. Current techniques are based on the electrical conductivity of the fluid present onto the pavement. They have limitations, induce constraints, with uncertainty up to 50 %. A poor knowledge of this residual amount does not allow a proper use, any improvement of road user safety, any cost reduction nor a reduction of the environmental impacts.

This study deals with a remote optical spectroscopic tool to measure the amount of residual de-icer. The results have shown many perspectives. A portable device has detected and precisely distinguished several ones. The analysis of the measured signal has conducted to the concentration of the fluid on the pavement surface, along with its associated freezing point.

## KEYWORDS

RESIDUAL DE-ICER / WINTER MAINTENANCE / REMOTE MEASURMENT

## 1. INTRODUCTION

The use of de-icers is one of the cornerstone of winter maintenance as a contribution to road users safety. Treatments of road networks are undertaken considering weather conditions, organization of services and the traffic according to the importance of road network stretches **[1]**. Economical and environmental considerations are added to these ones. De-icers such as sodium chloride have a significant cost for road winter maintenance services, and their known impact onto the environment has conducted Canada to take some legal measures to properly use them. The combination of all these considerations has conducted many organizations to study the life cycle of de-icers, and therefore to optimize their use. Sodium chloride NaCl and at a lower level calcium chloride $CaCl_2$ are the ones mostly used in France. Details could be found in the literature **[2-5]**.

De-icers lower the freezing point of the aqueous solution on a pavement, and so maintaining a proper grip level for road traffic **[5]**. They avoid the occurrence of sliding phenomena according to given weather conditions. The knowledge of the residual amount of de-icer on a pavement, or of the freezing point of the liquid phase at its surface is part of the decision making process. Such knowledge could be considered as a direct information, but remains the consequence of what was previously applied. But one could also determine the residual de-icer amount and its evolution. This parameter is more easily apprehended by a road manager who has a direct influence on spreading operations, used for further freezing point determination. Poor weather conditions, traffic, fluid flows on pavements cause losses that need to be known to properly appreciate the amount to add onto to pavement.

The detection of this residual de-icer amount has shown important limits, along with operator safety issues. Current technologies are based on the measurement of the electrical conductivity of the fluid located onto the pavement to deduce the amount of de-icers **[6-12]**. They have mainy constraints, and uncertainties are great and up to 50 % **[13]**. Some other technologies exist, but do have mitigated results, or more or less adapted **[14-18]**. Without a proper knowledge of this residual amount, it is impossible to reach a proper use, to improve road safety, and to reduce their cost and their environmental impact.

The objective of this study is to investigate a remote optical spectroscopic tool to measure the residual de-icer amount on roads. The technique will be first briefly described, along with its advantages with respect to conventional tools. Then some results will be presented, with the numerous perspectives. A portable device based on this spectroscopic tool has conducted to the detection and the precise discrimination of several de-icers. The analysis of the materials response has allowed the extraction of the de-icer concentration within the fluid located onto the pavement, along with the associated freezing point. This work has lead to several patents and has been funded by a national research program.

## 2. BRIEF DESCRIPTION OF THE SPECTROSCOPIC TOOL

### 2.1. Some light and some answers

The spectroscopic tool is based on the recording of the characteristics of the vibrations of chemical bonds in a material submitted to an incident light. Atoms are constantly vibrating around their equilibrium position. These vibrations occur at specific frequencies for each group of atoms, the spectroscopic tool is able to measure.

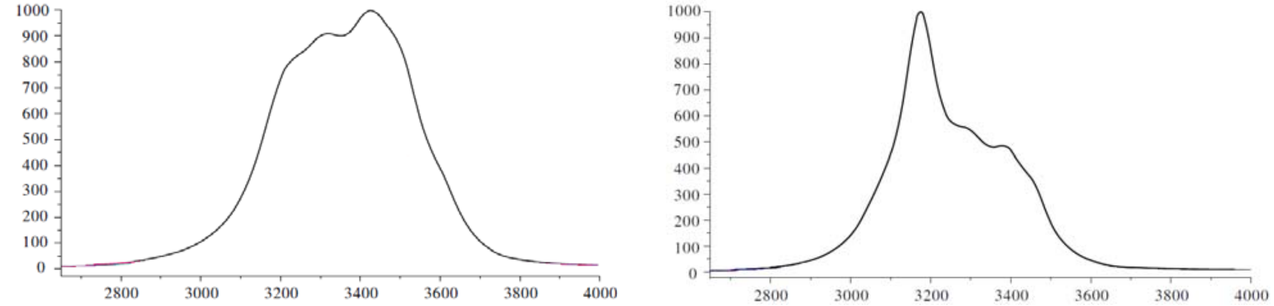
When a sample is submitted to a monochromatic light, atoms or ions vibrate at frequencies characteristic of the material. Part of the incident light is diffused at the same wavelength and another part at another frequency if an exchange took place with the material. If so, the energy difference between the incident light and this new one could be linked to the vibrations of the material atomic bonds. These vibrations are characteristics of the material structure and have very specific signatures. They carry information on the sample nature (structure, chemical composition), cristalinity, order degree, temperature ... with many advantages on the material analysis.

The material to study does not need any conditioning or specific preparation. It is only submitted to a monochromatic light which wavelength is selected according to the material and the research undertaken. The material behavior is collected on a CCD detector. The signal is characteristic of the chemical species and of the constraints they are submitted to.

Such tool has many advantages. The results are quickly obtained, even less than a second. This is a significant improvement with respect to devices embedded into road pavement where the determination of the quantity of residual de-icer could take several minutes. The information can now be obtained whatever the conditions are, in particular for temperature ones. Measurements could be done remotely or with contact according to the requirements of the situation. The tool is portable and cost effective.

### 2.2. Extraction of relevant signal for de-icers

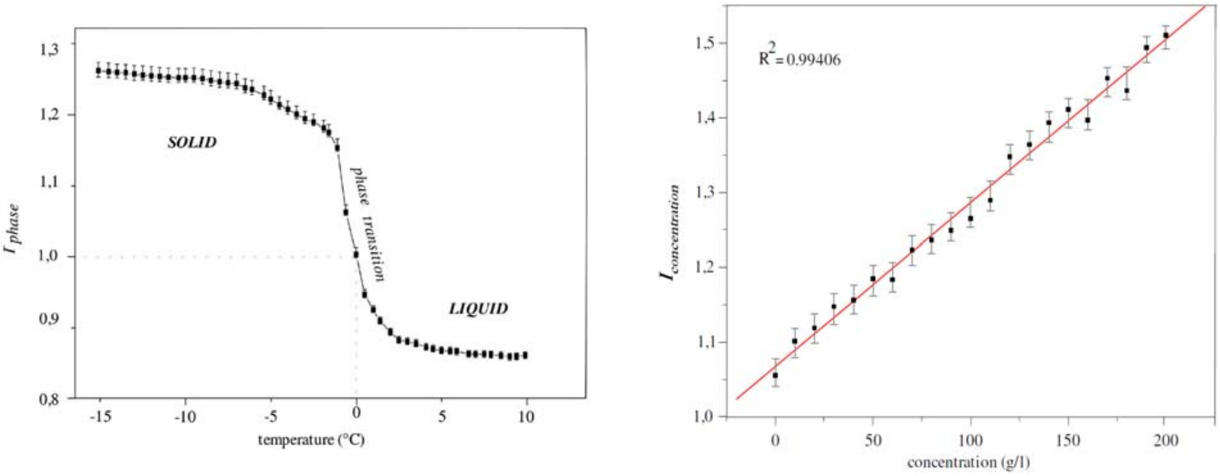
In this specific case, the studied material is water, with or without de-icer in it. The first step has consisted in the determination of the appropriate wavelength the material will be submitted to so as to obtain a signal. Once validated, the work was focused on the discrimination between the water solid and the liquid phases, then between brines phases. The results of these investigations are presented on Figure 1. The discrimination between the two water phases is well pronounced. An equivalent result was obtained in the case of brine.



(a) liquid water (b) ice

Figure 1 - Spectroscopic signatures of water
(normalized intensity of the signal as a function of wave numbers in $cm^{-1}$)

Then, based on theses measurements, the goal was to build a phase indicator $I_{phase}$ and another one dedicated to the de-icer concentration $I_{concentration}$ of the fluid located onto the pavement surface. Such a result was obtained extracting specific elements of water and the ones of de-icer from signatures as the ones on Figure 1. The indicators are illustrated on Figure 2. The one for concentration could be obtained from a linear regression as presented on Figure 2b, demonstrating the validity and the efficiency of the tool presented here.



(a) $I_{phase}$ parameter for the distinction of water phase

(b) $I_{concentration}$ parameter for a NaCl brine

Figure 2 - Indicators to identify the phase and the concentration the phase and the concentration of a brine solution used as de-icer

## 3. SEARCH AND DETERMINATION OF RESIDUAL DE-ICER

### 3.1. Elaboration of solid-to-liquid phase transition curves

Road slipperiness is due to the presence of a fluid on its surface, but it depends on its phase (liquid or solid). De-icers are used to obtain liquids at temperatures below 0°C, and down to -20°C when it comes to saturated NaCl brines. Nevertheless, poor weather conditions and traffic are greatly affecting de-icer residual quantity **[4, 5, 7-11]**. Therefore, some de-icer might provide a freezing point when it is applied but the targeted freezing point will change based on the meteorological and the traffic conditions. One might need to know the fluid phase as a function of its de-icer concentration and its temperature. Such phase determination is usually done with literature data, or with a standard protocol such as the one provided by ASTM D 1177–07 **[19]**.

A database was built with the analysis of measurements obtained with the spectroscopic tool, and that could be compared to phase diagrams. A variation with temperature of a phase index $I_{phase}$ for NaCl brines with concentrations ranging between 0 g/l and near saturation is given on Figure 3. Such results could be obtained with other de-icers (acetate, ...).

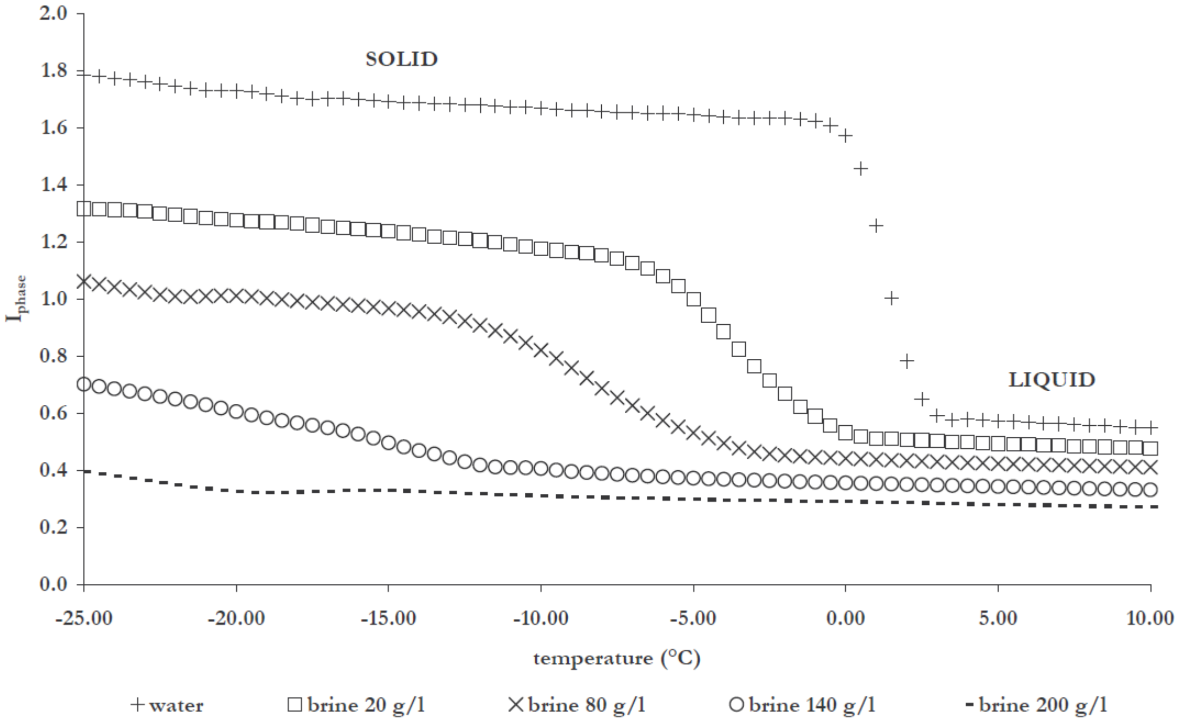


Figure 3 - Solid-liquid phase diagram for NaCl brines

### 3.2. Measurements simulating field conditions

A climatic chamber was used to evaluate the ability of the spectroscopic tool to operate in conditions close to field ones. Focus was put on the following topics: influence of the pavement, effect of conventional road pollutants, monitoring of de-icer solubility, blind test for concentration determination. The experimental setup is described on Figure 4.

(a) experimental setup
in the climatic chamber

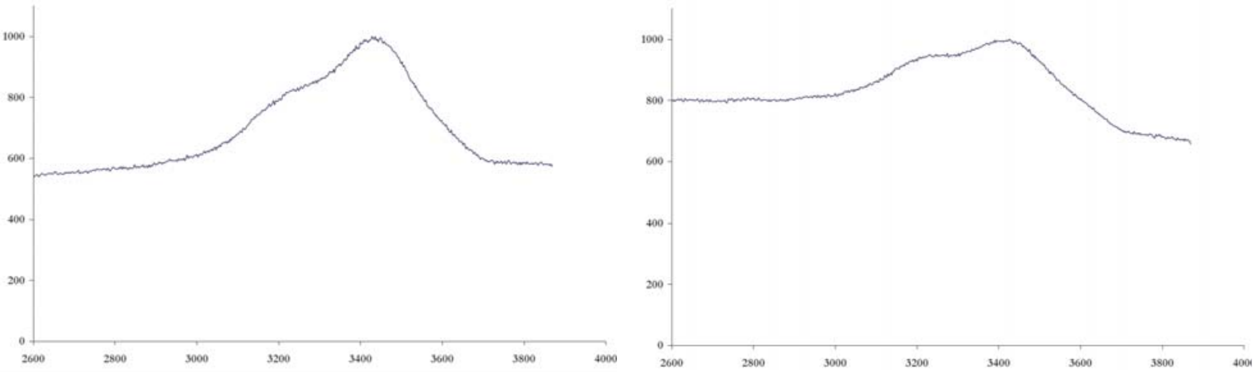
(b) PC and control panel
of the spectroscopic tool

Figure 4 - Experimental setup for the remote determination of residual de-icer

*Pavement influence*

The objective was to check that the presence of a pavement upon which the brine is applied did not affect the signal up to the point no analysis was possible. NaCl brines with concentrations ranging between 10 and 200 g/l were applied on an asphalt concrete pavement at temperatures from -17°C to 5°C, such as the ones met in winter maintenance. A similar work was done with potassium acetate brines.

The presence of asphalt concrete did not interfere with the signal. Results are correct and can be analyzed after numerical analysis (filtering, noise reduction, ...). Obtained signatures are presented on Figure 5 and are similar the ones obtained on Figure 1.



(a) NaCl brine
at 200g/l and -17°C

(b) NaCl brine
at 100 g/l and -7°C

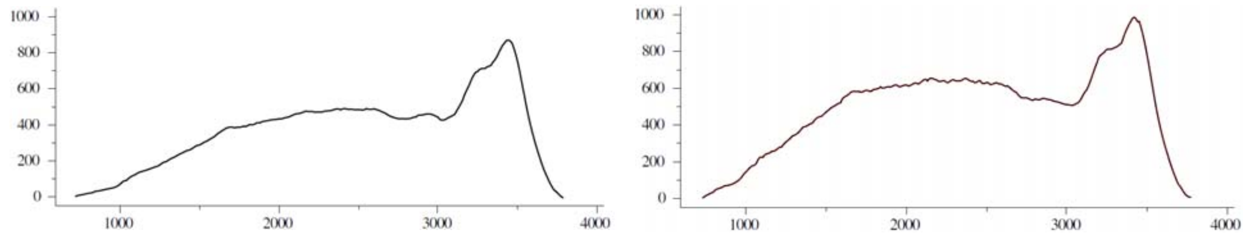
Figure 5 - Spectroscopic signatures of de-icers brines applied on asphalt concrete (normalized intensity of the signal as a function of wave numbers in cm$^{-1}$)

*Conventional road pollutants and residual de-icer quantity determination*

Pavements are collecting many pollutants from vehicles circulating on their surface. Among the most common ones, one can quote fuels, used motor oil; cooling liquid or braking fluid. Their quantities could vary a lot from one place to the next on an itinerary, and in volume on a spot of a same itinerary.

To evaluate the influence of such pollutants on the signal collected by the spectroscopic tool, different mixtures of brine and pollutants quoted before have been manufactured. A 140 g/l NaCl brine and a 114 g/l brine were considered. 3 ml of pollutant was added to obtain a 30 ml of solution for each selected pollutant. In the case of hydrocarbons, the mixture was vigorously mixed to get an homogeneous solution. A high quantity of pollutant was chosen so as to ensure the absence of incidence of these pollutants on the relevant information from de-icers. Tests were run at -12°C.

As with brines applied on a road pavement, the large amount of pollutants did not interfere with the detection of brine. Nevertheless, the braking fluid caused an additional signal, but the relevant part due to the brine can still be analyzed, as it was the case for the other pollutants, and illustrated on Figure 6.



(a) NaCl brine with gas

(b) NaCl brine with used motor oil

Figure 6 - Spectroscopic signatures of NaCl brines at -12°C,
applied on asphalt concrete in the presence of different pollutants

*Kinetics of de-icer dissolution*

As stated by Kaufmann in his book on NaCl **[5]**, a de-icer is only efficient once in solution. But de-icers are often applied as dry salt, or best as a mixture of brine and dry salt. Weather conditions, and relative humidity in particular, current precipitations and the ones to come onto the pavement **[20]** affect the time necessary to generate the brine from the de-icer applied.

A specific test was then undertaken. A defined amount of 100 g/l NaCl brine was applied on a surface. Some dry salt was immersed in the brine, outside the zone were the spectroscopic analysis was done. The whole set was installed in a climatic chamber at a temperature around -10°C. A data acquisition process was developed to monitor the spectroscopic response, air and surface temperature at a 1s time step. The brine and dry salt amounts are such that a full dissolution of the dry salt would provide saturated brine in these given conditions. The change in brine concentration with time was then monitored, and is shown on Figure 7.

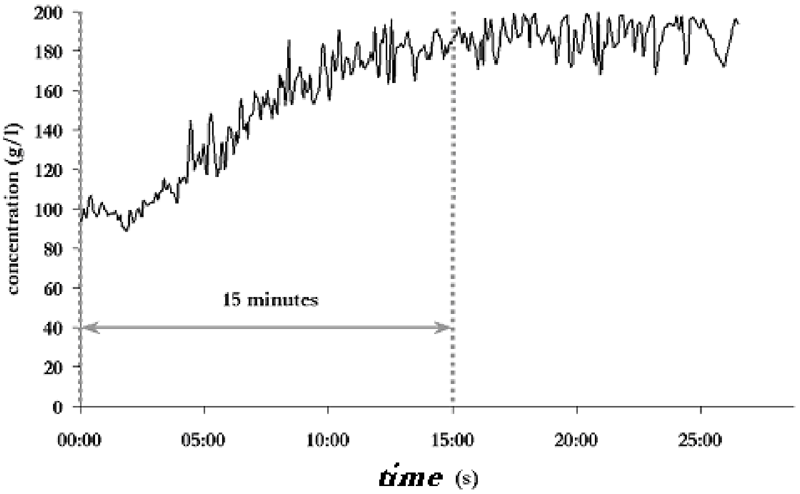


Figure 7 - NaCl brine concentration evolution with time
around -10°C in the presence of dry salt

Two things could then be obtained from the analysis. First the dissolution of dry salt was not immediate and needed long minutes that could be precisely estimated now. Such time is a precious piece of information in winter maintenance since it would provide winter services when the application of a de-icer might have reached its optimal efficiency. The other point is the ability of the device to collect data at a fast pace, even with the current 200 g/l limit, which correspond to the last value of the database generated for the concentration determination, and which Figure 3 is an illustration. This upper value can be easily overtaken.

Road managers are commonly using the amount of de-icer applied on a road in g/m². That is the way spreaders are set. Nevertheless, the determination of this amount could be obtained once the one of water on road pavement is known. According to Livet **[4]**, the amount of water that could be stored on an asphalt concrete is 200 g/m². With a specific mass of $10^6$ g/m$^3$, it corresponds to a 0.2 mm water film thickness. It is then possible to establish the de-icer amount on the road pavement. The spectroscopic tool is then able to run blind measurements of residual de-icer quantity on a road pavement on the basis of a known asphalt concrete, or on the hypothesis of the amount of water a pavement is able to store on its surface.

## 4. CONCLUSION

The spectroscopic tool described and presented in this study was able to run a remote measurement of residual NaCl as de-icer on a road pavement. The tool was validated for other de-icers. The process could be run with contact or remotely, is fast with results within a second. Systematic measurements have allowed building solid-to-liquid phase transition diagrams on extended temperatures ranges and on brines concentrations ones. The spectroscopic response was not affected by the pavement asphalt concrete, or by any usual road pollutants tested. Coupling this tool with a surface temperature measurement device, residual de-icer quantity was determined without any knowledge of what was previously applied. Therefore, the application of some de-icer by a winter service vehicle taking into consideration the amount of residual de-icer could become a reality in a near future.

## REFERENCES

[1] Viabilité hivernale. Approche globale. Guide méthodologique (2009). Document SETRA. 36 p
[2] Renck A.-S., Muzet V., Joly L., Livet J. (2002) Etude de l'action des fondants utilisés en viabilité hivernale sur la corrosion des métaux. Dossier 2002-D64-0030, 69 p.
[3] The use of selected deicing materials on Michigan roads (1993): Environmental and economic impacts. 104 p.
[4] Livet J. (1998). Fondants routiers. Journée thématique. 21 p.
[5] Kaufmann D. W. (1960). Sodium chloride. The production and properties of salt and brine. ACS monograph 145. ISSN 0065-7719. 743 p. Hafner Publishing Company, Inc.
[6] Appareil de mesure de la quantité de chlorure présente sur la route. SOBO 20 (2004). Manuel d'utilisation DV.00734.4-B. 23. 9 p.
[7] Livet J. (1994). "Evaluation de l'entraînement des fondants routiers par le trafic. Expérimentation RN 74". Projet "Météorologie routière" AER 1.90.03.4, dossier 94/0013. 5 p.
[8] Blomqvist G., Gustafsson M. (2004). "Patterns of Residual Salt on Road Surface. Case Study". Proceedings of "6th International Symposium on Snow Removal and Ice Control Technology", Spokane, Washington. Transportation Research Circular E-C063: Snow Removal and Ice Control Technology, pp. 602-608.
[9] Gustafsson M., Blomqvist G. (2004). "Modeling Exposure of Roadside Environment to Airborne Salt. Case Study". Proceedings du "6th International Symposium on Snow Removal and Ice Control Technology", Spokane, Washington.. Transportation Research Circular E-C063: Snow Removal and Ice Control Technology, pp. 296-306.
[10] Hunt C., Mitchell G. F., Richardson W. (2004). "Field Persistence of Anti-Icing Sodium Chloride Residuals". Proceedings du "6th International Symposium on Snow Removal and Ice Control Technology", Spokane, Washington.. Transportation Research Circular E-C063: Snow Removal and Ice Control Technology, pp. 609-622.
[11] Garrick N. W., Nikolaidis N. P. (2002), Luo J. A Portable Method to Determine Chloride Concentration on Roadway Pavements. Projet n° 97-1, 43 p.
[12] Gayle M., Hunt C., Richardson W. (2003). "Evaluation of ODOT Roadway/Weather Sensor Systems for Snow and Ice Removal Operations. Part III : Optimization of Salt Brine Pre-Treatment Application Rates and Frequency". Rapport final FHWA/OH-2003/08C.
[13] Raukola T, Kuusela R, Lappalainen H, Piirainen A. (1993). Anti-Icing Activities in Finland : Field Tests with Liquid and Prewetted Chemicals. Transportation Research Record, Issue: 1387, pp 48-56.
[14] Jeger P. (1996). New Sensor Principle for Determining the Condition of Roads. Proceedings of the 8th SIRWEC Conference, Birmingham (U.K.). pp.193-195.
[15] Paulsen T.A., Schmokel P. (2004). "Laser Road Surface Sensor – LRSS". Proceedings of the 12th SIRWEC Conference, Bingen (Germany).
[16] Yamada M., Oshima T., Ueda K., Horiba I. (2003). Yamamoto S. "A Study of the Road Surface Condition Detection Technique for Deployment on a Vehicle". JSAE Review, 24, pp. 183-188.
[17] http://www.rock.fr/sels-routiers/autres-produits/
[18] Dinnat E. P. (2003). De la détermination de la salinité de surface des océans à partir de mesures radiométriques hyperfréquences en bande L. Thèse de doctorat. 271 p.
[19] Standard Test Method for Freezing Point of Aqueous Engine Coolants. norme ASTM D 1177 – 07. 3 pages
[20] Marchetti M., Livet J., Poissonnier S., Diop I.(2006). Brines concentration evolution with climatic conditions. Effect of temperature and relative humidity, precipitations and traffic. Proceedings of the 12th PIARC conference, Torino (Italy)