

Fluorescence of road salt additives: Potential applications for residual salt monitoring

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ABSTRACT

Fluorescence Techniques are used to identify the fluorescence signal emitted from a molasses based de-icer mixed with rock salt. Tests have shown that molasses based de-icing products have a unique fluorescence signal, the peak intensity of which excites and emits at 340 and 420 nm respectively and is unaffected by changes in temperature. The fluorescence signal is easily identifiable at temperatures as low as -8°C, and the intensity of the signal has been found to be reasonably constant over the temperature range 0 to 5°C, which is most associated with the marginal nights in the UK where there is a chance a road surface may freeze. Within this temperature range the intensity of the fluorescence signal could be used to quantify salt concentrations. Remote sensing tests of the same fluorescence signal using a fibre optic probe have revealed difficulties in applying such a technique in a road environment. The potential applications of this research to road weather and other scientific fields are discussed.

Keywords: road weather, molasses based de-icer, fluorescence, marginal nights, salt concentrations

1. INTRODUCTION

The main purpose of a Road Weather Information System (RWIS) is to reduce the cost to Highway Authorities of keeping roads free of ice and snow whilst also making roads easier and safer to travel on [4]. In RWIS, information about road surface temperature (RST), surface wetness, freezing point temperature (FPT) and residual de-icing chemicals is linked with atmospheric measurements and synoptic weather information to give a prediction of whether or not roads will require chemical treatment in the following hours to prevent them from icing over. De-icing chemicals work by lowering the freezing point of water, and the most common type of chemical used for ice prevention on roads is sodium chloride (NaCl), commonly referred to as rock salt. NaCl is used in large quantities around the world, with approximately 15 million tonnes of salt spread each year in the United States. In the United Kingdom rock salt sales in very cold winters have been known to reach 2 million tonnes, but the average is closer to one million tonnes per winter [6]. The costs of salting to Highway Authorities is therefore high, and any method that can accurately measure residual salt on a road surface has the potential to save Highway Authorities huge sums of money every year by reducing the wastage that results from over-salting.

2. BACKGROUND

Traditional passive road sensors provide an estimation of residual salt via measurement of the electrical conductivity of surface water and the use of mathematical algorithms. Active road sensors freeze the aqueous solution laying on the surface by artificial means, thus providing a truer indication of the freezing temperature of the road surface. However, both types of sensor have a fundamental flaw in that neither can be truly representative of the road surface they are embedded in since they are only sampling a very small area of the surface (typically 1cm in diameter). A more representative measurement should include a much larger surface area, something that is impossible with current embedded road sensor designs.

Most European countries use wetted salt or brine on their roads since the drier continental climate prevents dry salt from going into solution, whereas the more humid maritime climate in the United Kingdom usually enables dry rock salt to go into solution when spread. Due to the longer term corrosive impacts of NaCl on vehicles and road structures (particularly bridges), the costs of which are estimated to be in the region of £100 million in the United Kingdom alone [5], numerous attempts have been made to develop more environmentally friendly chemicals for use in winter road maintenance. Recently much attention has focused on the use of molasses

based products combined with rock salt, which in research trials in the United Kingdom have been shown to reduce the corrosive effect of salt by up to 50%. This is comparable to urea, ethylene glycol and potassium acetate, but at a considerably reduced cost [6]. A number of Highway Authorities in the United Kingdom have been testing molasses based de-icing products mixed with rock salt over the past few winters, and initial results have shown benefits in terms of faster ice melting and more targeted spreading of salt, and there is a general consensus that such products have clear operational benefits and longer term anti-corrosive advantages.

With the increased use of molasses based de-icers on roads likely in the future, a new line of research has been undertaken which uses modern techniques to identify the fluorescence signal emitted from a molasses based de-icer mixed with rock salt. Since molasses based de-icing products are typically premixed with rock salt at a known weight for weight ratio, theoretically it should be possible to identify actual salt concentrations from the intensity of the fluorescence signal.

3. METHODOLOGY

3.1 Identification of fluorescence signature

The fluorescence signature of the molasses based product was first of all identified. Tests were carried out in a laboratory using a Varian Cary Eclipse fluorescence spectrophotometer. Due to the concentrate nature of the molasses, dilutions were required to prevent inner filtering effects from obscuring the fluorescence signal. Initial dilutions revealed an intense fluorescence signal, the centre of which was exciting and emitting at approximately 340 nanometres (nm) and 420 nm respectively. A number of dilutions were run with distilled water until no fluorescence signal was obtainable. With the photomultiplier tube voltage in the fluorescence spectrophotometer set at 725 V, a fluorescence signal from the molasses de-icing product was detectable down to a dilution of $10E^{-6}$.

In order to replicate typical conditions which might be found on a road surface, samples of rock salt pre-mixed with the molasses were diluted with road run-off water at a rate of 10 g of salt per litre of water. This assumes a typical surface water depth on a road surface of 1mm, which equates to 10 g/litre of water based on a salting application rate of 10 g/m². Based on the weight for weight ratio of the molasses and rock salt mixture, this equated to a typical dilution on a road surface of approximately 1:4500. The fluorescence signal detectable with this dilution was then identified for three different types of rock salt doped with the same molasses de-icing product, know here as Salt A, Salt B and Salt C, all three of which are commonly used in de-icing operations in the United Kingdom.

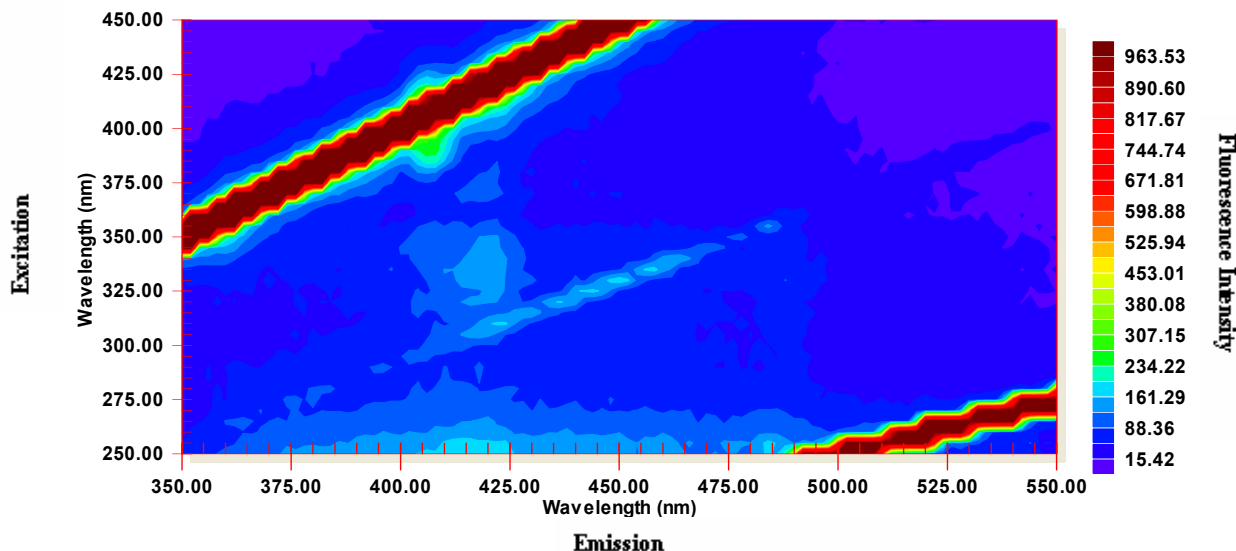


Fig. 1. Excitation-Emission Matrix for road surface water with no molasses de-icing product.

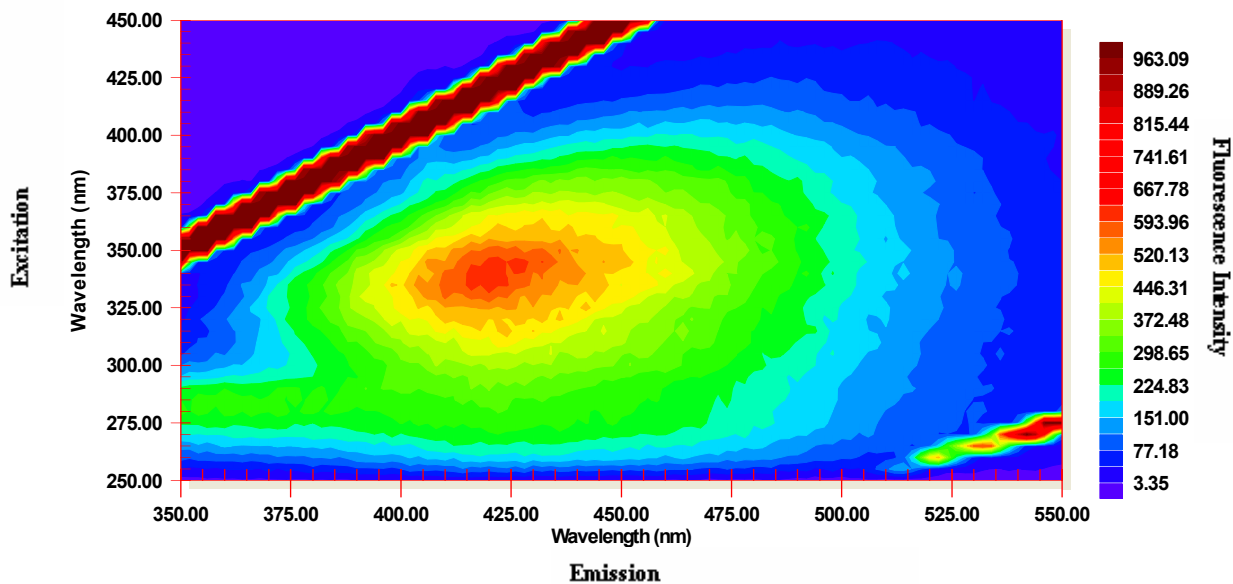


Fig. 2. Excitation-Emission Matrix for Salt A diluted with road surface water – dilution 1:4500.

Figures 1 and 2 above display Excitation-Emission Matrices (EEMs) for the fluorescence signal of road surface water (figure 1) and the diluted doped salt (figure 2). EEMs are simply a graphical display of a fluorescence signal's intensity of emission across a specified wavelength band for a particular excitation wavelength, and are useful for identifying the peak excitation-emission wavelengths of a signal (i.e. the wavelengths at which the signal is most intense). As the figures above show, the diluted doped salt (figure 2) displays a strong fluorescence signal greater than anything naturally present in road surface water (figure 1). The EEM for the diluted doped salt reveals that peak intensity of fluorescence is found at an excitation wavelength of approximately 340 nm and an emission wavelength of approximately 420 nm, which was consistent for all three salt types. In fact, the EEMs for Salt B and Salt C were the same except for variations in the intensity of the signal, most likely due to slight inconsistencies in the weight for weight mixture of molasses to salt between the three different salt types. Fluorescence which occurs at these wavelengths is longer wavelength fluorescence, often called fulvic-like, with excitation between 300-340 nm and emission between 400 and 460 nm. Fluorescence of this nature is typically ascribed to aromatic moieties (groups of atoms that form a molecular unit or molecular ion) in the high molecular weight dissolved organic matter fraction which is relatively recalcitrant (resistant to breakdown) [3].

3.2 The effects of temperature

The intensity of a fluorescence signal reduces (quenches) with increasing temperature [2]. A rise in temperature increases the likelihood that electrons within a molecule will fall back to the ground state by a radiationless process, and the extent to which thermal quenching occurs relates to the exposure of the fluorophore to this energy source [1]. Fulvic-like fluorescence has been shown to exhibit quenching of between ~20 and 25% for river and waste water samples over a 35 degree temperature range from 10°C to 45°C, and changes in sample temperature have not been found to alter the excitation or emission wavelengths of the fluorescence centres [1].

Tests at varying temperatures were carried out with the three diluted doped salts to determine how their fluorescence changes as temperature changes. The Cary Eclipse fluorescence spectrophotometer is equipped with a multicell holder with Peltier temperature controller enabling the measurement of EEMs at a variety of precisely controlled ($\pm 0.1^\circ\text{C}$) temperatures. Each EEM was generated by scanning excitation wavelengths from 250-450 nm at 5 nm steps, and detecting the emitted fluorescence between 350 and 550 nm. The three diluted doped salts were sampled at various temperatures from 20°C down to -8°C, and the excitation and emission wavelengths of the fluorescence centre together with the fluorescence intensity were identified for each temperature.

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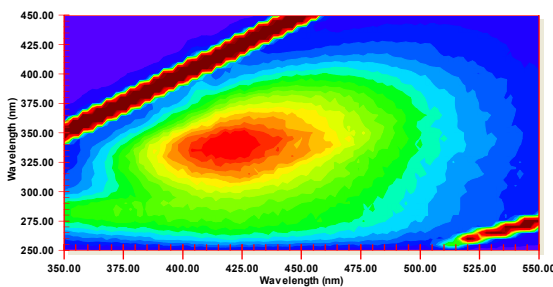
Temperature (Deg C)	Peak Excitation Wavelength (nm)			Peak Emission Wavelength (nm)			Peak Fluorescence Intensity		
	Salt A	Salt B	Salt C	Salt A	Salt B	Salt C	Salt A	Salt B	Salt C
20	342	338	340	421	420	423	646	459	608
15	342	338	340	423	422	422	678	465	633
10	341	340	337	421	419	422	701	488	656
5	341	340	342	420	424	419	764	508	718
0	340	338	340	421	423	420	789	534	737
-1	342	340	341	421	422	420	732	539	674
-2	341	339	340	419	421	421	522	471	599
-5	340	340	340	420	422	417	496	391	498
-8	340	340	341	420	421	420	582	498	621

Table. 1. Fluorescence characteristics of diluted Salts A, B and C at various temperatures.

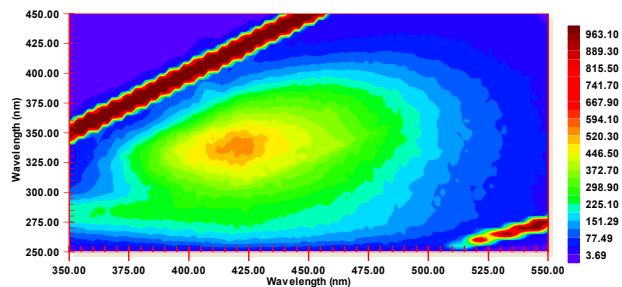
As can be seen from the data in Table 1, the peak excitation and emission wavelengths of the fluorescence centres were consistent as the temperature changed, which supports the findings by Baker [1]. As for the change in fluorescence intensity, the diluted Salt A increased from 646 at 20°C to 789 at 0°C, an increase of 18%. This compares to an increase of 14% for Salt B and 17.5% for Salt C over the same temperature range.

The fluorescence intensity of all three diluted doped salts began to decrease as the temperature fell below 0°C. Visual inspection at -2°C indicated that the samples were starting to freeze, which explains the decrease in fluorescence intensity that was observed. As the doped solutions begin to solidify, more energy is required to excite the molecules and make them fluoresce at the same intensity as before. Since no additional energy was being supplied, the fluorescence observed was that from the remaining unfrozen molecules. Thus, the fluorescence intensity observed decreased as the solutions began to freeze, but the amount of signal loss was less than expected and with all three samples the fluorescence signal was still detectable once the solutions had frozen.

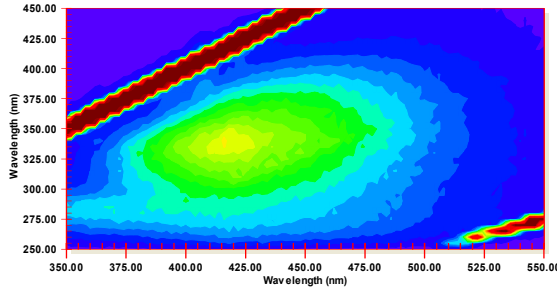
Figures 3a to 3d show the signal loss for the diluted Salt C as the temperature was lowered from 0°C to -8°C. In figure 4d it can be seen that the intensity of the signal starts to increase again, which relates to scattering affects resulting from light reflecting off the surface of the frozen sample. Similar scattering affects also occurred with the diluted Salt A and Salt B samples.



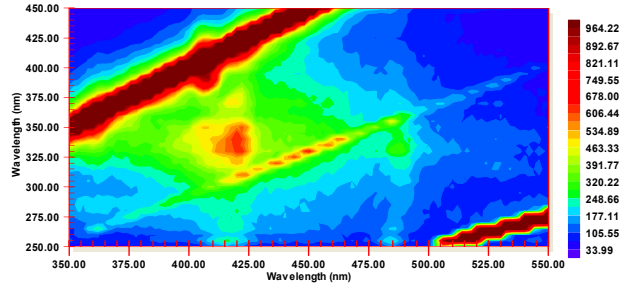
3a. EEm for Salt C at 0°C



3b. EEm for Salt C at -2°C



3c. EEm for Salt C at -5°C



3d. EEm for Salt C at -8°C

Fig. 3a to 3d. EEMs for diluted Salt C at a range of temperatures between 0°C and 8°C (left y axis = excitation wavelength, x axis = emission wavelength, right y axis = fluorescence intensity).

With regards to road salting in the UK, marginal nights are the most problematic where the road surface may freeze, most notably within the temperature range 0 to 5°C. Nowadays with the increased liability of Highway Authorities in ensuring that highways are kept free of snow and ice, if temperatures are forecast to fall below 0°C Highway Authorities in the UK are likely to salt roads as a precautionary measure regardless of the rest of the forecast. Therefore, focusing on the temperature range from 0 to 5°C, the difference in the fluorescence signal intensities over this temperature range for each of the three diluted doped salts are similar, these being 25 (Salt A), 26 (Salt B) and 19 (Salt C). This equates to a variation of ± 2.5 to 5% over the three samples. If we account for an instrument accuracy of 3%, we find that the fluorescence intensity over the 0 to 5°C temperature range is reasonably constant, with only a small amount of thermal quenching occurring as the temperature increases. This suggests that between 0 and 5°C it is possible to relate the intensity of fluorescence to the amount of salt in the sample, allowing for the margins of error quoted above.

4. REMOTE SENSING

To apply such a technique within a RWIS would require the fluorescence signal from the road surface to be remotely sensed using a sensor mounted several metres from the road surface, in order to achieve large surface area coverage. A fibre optic probe attachment for the fluorescence spectrophotometer was used to remotely measure the fluorescence signal of the dry doped salts. Figure 4 displays the signal intensity measured at various distances from the surface of Salt A.

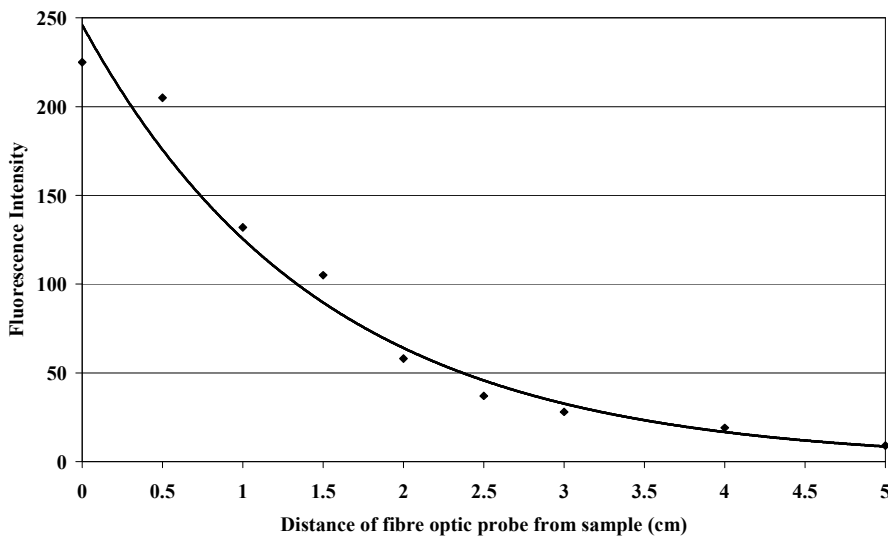


Figure 4: Fluorescence signal detectable from Salt A (2 grams) with the fibre optic probe.

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As figure 4 shows, the loss of signal with increasing distance from the fluorescence source demonstrates the inverse square law, indicating that the fluorescence is being radiated spherically in all directions. Similar intensity losses were observed for Salt B and Salt C, with up to 96% of the signal strength lost at a distance of just 5cm from the fluorescence source. The fluorescence intensity of the diluted doped salt samples (1:4500) was also measured by applying 2 ml of diluted doped salt uniformly onto a glass slide, and sampling the fluorescence with the fibre optic probe whilst the samples were wet and after they had dried. As table 2 shows, the fluorescence signals obtained from the diluted samples were relatively weak, and when allowed to dry as would occur on a road surface the signal was virtually undetectable considering the background fluorescence for the glass slide was between 8 and 12 intensity units.

Salt Type	Fluorescence Intensity (Wet)	Fluorescence Intensity (Dry)
Salt A	44	18
Salt B	39	16
Salt C	36	15

Table. 2. Fluorescence signal detectable from wet and dry diluted samples of Salt A, Salt B and Salt C.

5. OTHER POTENTIAL APPLICATIONS

A road surface could be excited with much more energy than the fibre optic probe and spectrophotometer used in these experiments are capable of, possibly through the use of a very large blue LED array. More research would be required to investigate such possibilities, but given the magnitude of signal loss identified in these experiments over a distance of only a few centimetres, with current technology it is unlikely that a cost effective sensor can be developed that is capable of exciting and detecting the emitted molasses fluorescence signal from several metres away. However, if the improvements made in LED technology over recent years continue, the development of such a sensor may be feasible sometime in the future. An alternative approach at the present time could possibly involve mounting a sensor on the front of a gritting lorry, thereby reducing the distance between the sensor and the road surface to only a few centimetres. Although such an approach would provide smaller surface area coverage, it could significantly reduce signal loss and would introduce the possibility of using alternative energy sources for exciting the fluorescence, such as xenon bulbs. It is envisaged that such a sensor could form part of an "intelligent salting system" on a gritting lorry, where data on surface residual salt is fed into a microprocessor which uses the data to continually adjust the rate of salt application from the rear of the vehicle to match the surface requirements. The fluorescence techniques discussed may also have alternative applications in fields such as environmental monitoring of water quality from road run-off. This research has shown that molasses based de-icing products have a unique fluorescence signal, which makes them easily identifiable and quantifiable in road run-off water using the laboratory fluorescence techniques discussed in this paper.

6. CONCLUSION

Research has been undertaken which uses modern techniques to identify the fluorescence signal emitted from a molasses based de-icer mixed with rock salt. In laboratory tests it has been shown that molasses based de-icing products have a unique fluorescence signal whose centre is unaffected by changes in temperature. The intensity of this fluorescence signal was found to be reasonably constant over the temperature range 0 to 5°C, which is most associated with marginal nights where there is a chance a road surface may freeze. Within this temperature range the intensity of the fluorescence signal can be used to quantify molasses concentrations, but further work will be required to ensure that these are proportional to the salt concentrations. Remote sensing of the same fluorescence signal has been carried out in a laboratory using a fibre optic probe, with the results showing that signal losses due to the fluorescence being radiated spherically in all directions are as great as 96% over a distance of only 5cm. In addition, the fluorescence signal from dry samples of diluted doped salt was virtually undetectable when remotely sensed with a fibre optic probe. Given this large loss of signal when remotely sensed, it is unlikely that a cost effective sensor can be developed that is capable of exciting and detecting the emitted molasses fluorescence signal from several metres away. To overcome the problem of signal loss, an alternative approach could involve a sensor being mounted on the front of a gritting lorry just a few centimetres from the road surface. Such a sensor would require a relatively large energy source to produce a detectable fluorescence signal, but options such as xenon bulbs could be considered with such a system. The laboratory

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techniques discussed may also have alternative applications, in particular the use of fluorescence techniques to identify and quantify concentrations of molasses based de-icers in road runoff.

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