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

D S Hammond[1,2], L Chapman[2], A Baker[2], J E Thornes[2] and A Sandford[1]

[1] Campbell Scientific Limited, Shepshed, Loughborough, Leicestershire, LE12 9GX, UK
[2] University of Birmingham, Edgbaston, Birmingham, B15 2TT, UK

E-mail: david@campbellsci.co.uk, andrew@campbellsci.co.uk, l.chapman@bham.ac.uk, a.baker.2@bham.ac.uk and j.e.thornes@bham.ac.uk

Abstract

Residual salt monitoring on roads is an ongoing challenge for winter maintenance engineers. Traditionally, estimates are made by measuring the electrical conductivity of the surface water, but this approach is often unreliable and ultimately site specific. In this paper, 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. Total organic carbon analysis has revealed a relationship between molasses and salt concentrations, meaning the fluorescence signal from the molasses could be used to quantify salt concentrations. Remote sensing tests of the 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 concentration, residual salt

(Some figures in this article are in colour only in the electronic version)

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 (Thornes 1991). 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 alone. 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 (Thornes
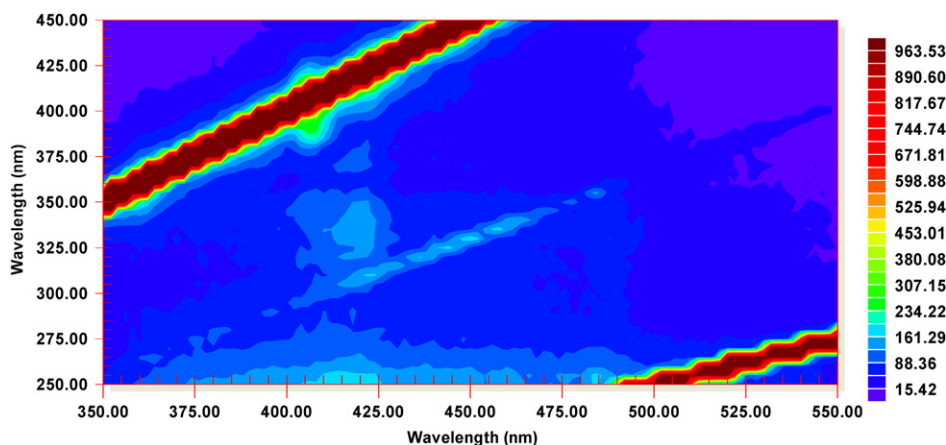
Figure 1. Excitation–emission matrix for road surface water with no molasses de-icing product (left *y* axis = excitation wavelength, *x* axis = emission wavelength, right *y* axis = fluorescence intensity).

2003). 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.

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 1 cm 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 in some countries, for example the United Kingdom, the more humid maritime climate 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 (Thornes 1996), 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 (Thornes 2003). 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. Indeed, 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 looking likely in the future, a new line of research has been undertaken which uses a technique 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, assuming an even distribution of molasses within the salt it should be possible to identify actual salt concentrations from the intensity of the fluorescence signal.

2. Methodology

2.1. 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 concentrated 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 ($\pm$3 nm precision). 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 10×10^{-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 1 mm, which equates to 10 g l^{-1} of water based on a salting application rate of 10 g m^{-2}. 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 salts A, B and C, all three of which are commonly used in de-icing operations in the United Kingdom.

Figures 1 and 2 display excitation–emission matrices (EEMs) for the fluorescence signal of road surface water (figure 1) and the diluted doped salt (figure 2). Scattered light
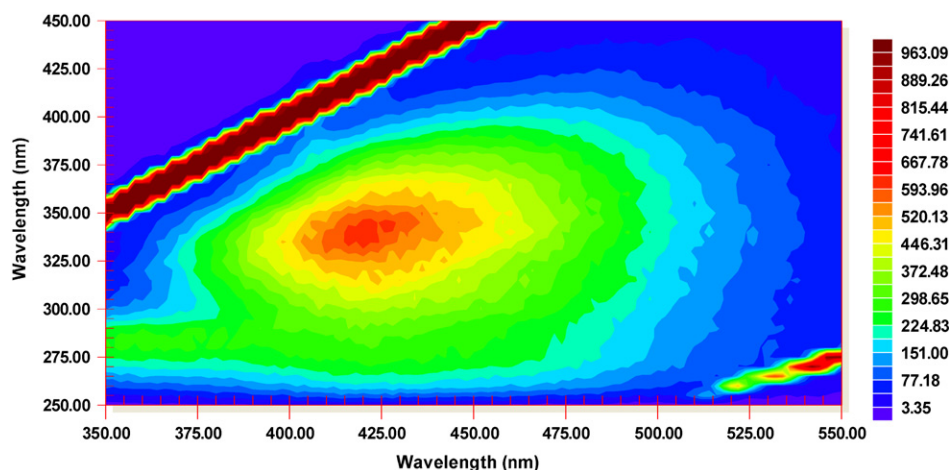
Figure 2. Excitation–emission matrix for salt A diluted with road surface water-dilution 1:4500 (left y axis = excitation wavelength, x axis = emission wavelength, right y axis = fluorescence intensity).

is visible as diagonal lines at excitation wavelength = emission wavelength and excitation wavelength × 2 = emission wavelength. No significant scatter is observed at the same location in optical space as the fluorescence from the doped salt. EEMs are simply a graphical display of a fluorescence signal 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 figures 1 and 2 show, the diluted doped salt displays a strong fluorescence signal greater than anything naturally present in road surface water. 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. Variations in the excitation wavelength between 300 and 350 nm had little affect on emission, with the emission wavelength of maximum intensity always occurring between 410 and 430 nm. Indeed, the EEMs for salts B and 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. Senesi *et al* (1989) have shown that fluorescence which occurs at these wavelengths is longer wavelength fluorescence, often called fulvic-like, with excitation between 300 and 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 resistant to breakdown (Leenheer and Croué 2003).

2.2. The effects of temperature

The intensity of a fluorescence signal reduces (quenches) with increasing temperature (Lakowicz 1999). 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 (Baker 2005). Fulvic-like fluorescence has been shown to

exhibit quenching of between ∼20 and 25% for river and waste water samples over a 35 °C 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 (Baker 2005).

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 (±0.1 °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.

As can be seen from table 1, the peak excitation and emission wavelengths of the fluorescence centres were consistent as the temperature changed, which supports the findings by Baker (2005). 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. 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 4(*a*) to 4(*d*) show the signal loss for the diluted salt C as the temperature was lowered from 0 °C to −8 °C. Note that scattered light could now interfere at very low temperatures (figure 4(*d*) has a third scatter line from light reflected from the ice crystals), but this scatter line does not overlap with the fluorescence and so can
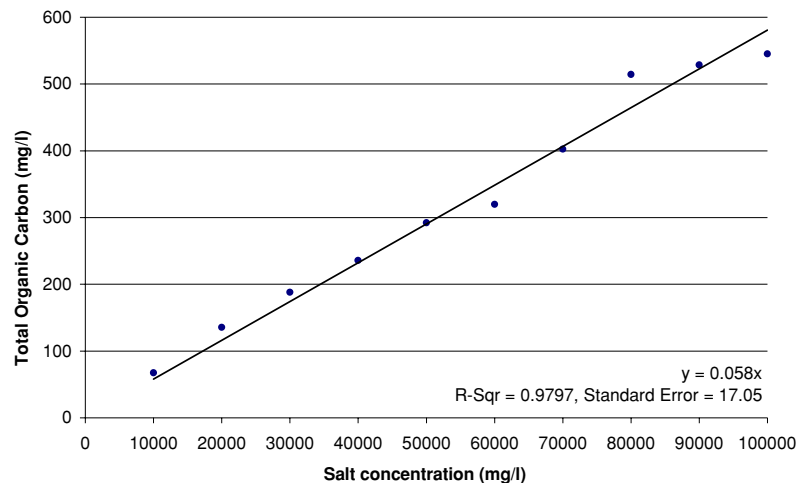
Figure 3. Regression analysis indicating the relationship between molasses concentration (via TOC analysis) and salt concentration.

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

Temperature (°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

be avoided with the correct choice of excitation and emission wavelengths. Similar scattering affects also occurred with the diluted salt A and salt B samples.

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 ±2.5–5% over the three samples. Accounting for an instrument precision of ±3 nm, 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 previously quoted.

2.3. Total organic carbon analysis

To ensure that a relationship exists between the concentrations of molasses (which is proportional to the fluorescence

intensity) and salt, samples of the doped salt were dissolved in deionized water at increasing concentrations from $10\,000$ mg l^{-1} to $100\,000$ mg l^{-1}. A total organic carbon (TOC) analyser was then used to identify the amount of TOC in each sample, and a regression analysis was performed on the resulting data (figure 3). As can be seen from figure 3, a clear relationship exists between TOC in the molasses and the concentration of salt, with the resulting regression equation giving a reasonably good indication of the amount of organic carbon/gram of salt.

3. Remote sensing

To apply the fluorescence techniques discussed 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 5 displays the signal intensity measured at various distances from the surface of salt A. Figure 5 shows that the loss of signal with increasing distance from the fluorescence source demonstrates an inverse square law, indicating that the fluorescence is being radiated spherically in all directions. Similar intensity losses were observed for salts B and C, with up to 96% of the signal strength lost at a distance of just 5 cm from the fluorescence
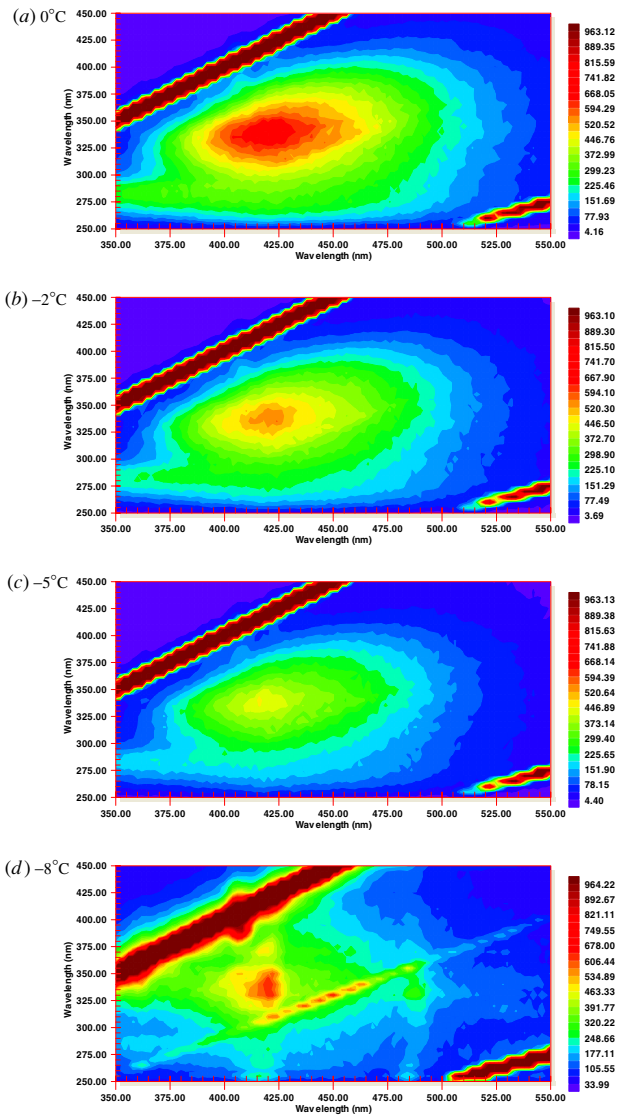
Table 2. Fluorescence signal detectable from wet and dry diluted samples of salts A, B and C.

Salt type	Fluorescence intensity (wet)	Fluorescence intensity (dry)
Salt A	44	18
Salt B	39	16
Salt C	36	15

Figure 4. 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).

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.

These results indicate that at the present time, such an approach for residual salt monitoring is limited. However, a road surface could be excited with greater 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. Any such system would require a method of keeping the sensor clean, possibly by blowing compressed
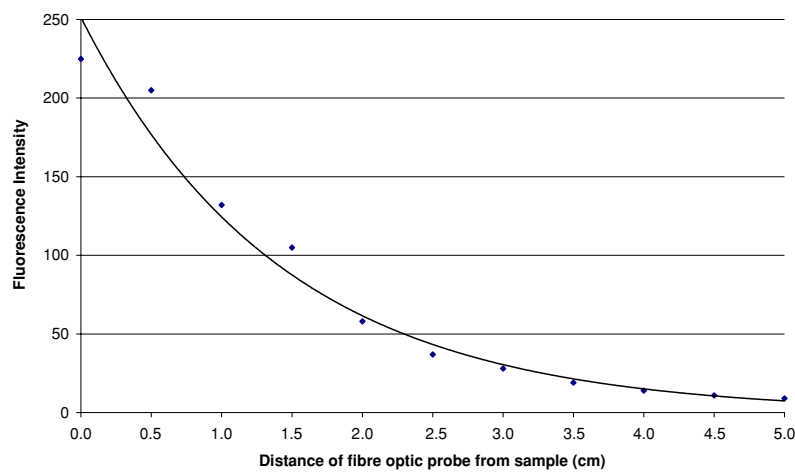

Figure 5. Fluorescence signal detectable from salt A (2 g) with the fibre optic probe.

air over the front of the sensor. 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 are 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. Interesting future research could include measuring the fluorescence lifetime of the molasses using a laser, although lasers have limited excitation wavelengths depending on the laser dye used. There is however a laser line at 348 nm, which would be ideal for lifetime works on the molasses.

4. Conclusions

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 signal was found to be reasonably constant over the temperature range 0 to 5 °C, and can be used to quantify both molasses and salt concentrations based on the fluorescence and TOC results obtained in this study.

Remote sensing of the fluorescence signal using a fibre optic probe has shown that signal losses due to the fluorescence being radiated spherically in all directions are as great as 96% over a distance of only 5 cm. 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 fluorescence signal from several metres away. Hence, this technology may be limited to sensors mounted on the front of the gritting fleet 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.

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