TECHNICAL NOTE

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Crystal Violet Lactone As a Security Marker for Fuels

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ABSTRACT: Crystal Violet Lactone (CVL) is normally used in carbonless copy paper. The reaction between CVL and polar substances such as silica gel produces a blue color. A novel use of CVL as a security marker in the larceny of fuel is described.

KEYWORDS: forensic science, crystal violet lactone

The larceny of fuels from large companies can lead to a considerable loss of revenue to the company over a period of time. In general the suspects can be narrowed down to a few once the larceny has been established.

A common method of apprehending the suspect or suspects is to add a marker to the bulk fuel supply and then to sample the fuel tanks of the individuals suspected to test for the presence of the marker. Some common markers used involve the addition of indicator chemicals such as phenolphthalein and/or thymolphthalein to the fuel. Visualization of this afterwards involves the addition of a basic solution and observing the color change of the aqueous layer.

This type of visualization is not suitable for field testing of the marked fuel as it would involve the police to carry quantities of hydroxide solution.

Other marker systems involve the use of fluorescent dyes with subsequent visualization by U.V.

We wish to describe the use of Crystal Violet Lactone (CVL) as a security marker. It can be shown to be easily visualized in the field and easily quantified in the laboratory.

Materials and Methods

A CVL (Aldrich, CAS Reg. No 1552-42-7) marker concentrate is prepared by dissolving CVL in 1 liter of fuel. The amount of CVL in the concentrate is dependant on the quantity of fuel in the bulk tank to which the concentrate is to be added. A final concentration of 8 ppm is suitable, that is, 8g of CVL per 1000 liters bulk fuel.

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Test mixtures of 0, 2, 4, 6 and 8 ppm of CVL in diesel oil were prepared. To 20 mL of each of the 5 samples was added 1 g of silica gel [Silica Gel 60G for thin layer chromatography, Merck]. The silica gel became blue in color on addition to the samples containing CVL. This mixture was stirred for 2 minutes with a magnetic stirrer. The spectrum of the suspension was measured in 1 cm cells versus unmarked diesel as reference on a UV/visible spectrometer (Shimadzu 160A). The absorbency was measured at the λmax at around 606 nm. An approximately linear graph was obtained when absorbency was plotted against concentration (Fig. 1).

A qualitative analysis was carried out by adding 1g of silica gel to 20 mL of marked diesel. The blue colored silica gel resulting was filtered and washed with hexane. The CVL adsorbed to the silica was leached by washing with 10 mL of methanol. This methanol solution was then colorless as was the silica gel. Spotting of the methanol solution on a TLC plate and using Toluene:Methanol:Acetone (20:2:1) as the mobile phase resulted in a blue spot. A spectrum of this blue spot was obtained using a TLC scanner (scanned from 370 nm-700 nm Shimadzu CS-930 TLC Scanner) and the resulting spectrum was similar to that obtained for the suspension. HPLC was run using a C18 reverse phase column with a mobile phase of 90/10 methanol/water and a flow rate of 1 mL/min on a Varian 5000LC equipped with a diode array detector. A peak at 3.4 minutes was found for an 8 ppm solution of CVL in methanol. An 8 ppm solution of CVL in diesel was extracted with silica, washed with hexane and then washed with methanol (as discussed). This extract was injected on to the column and a

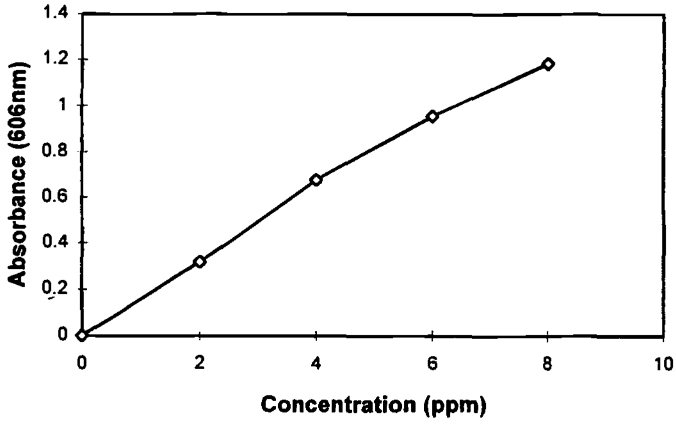

FIG. 1—*Calibration curve for CVL/silica gel suspension.*

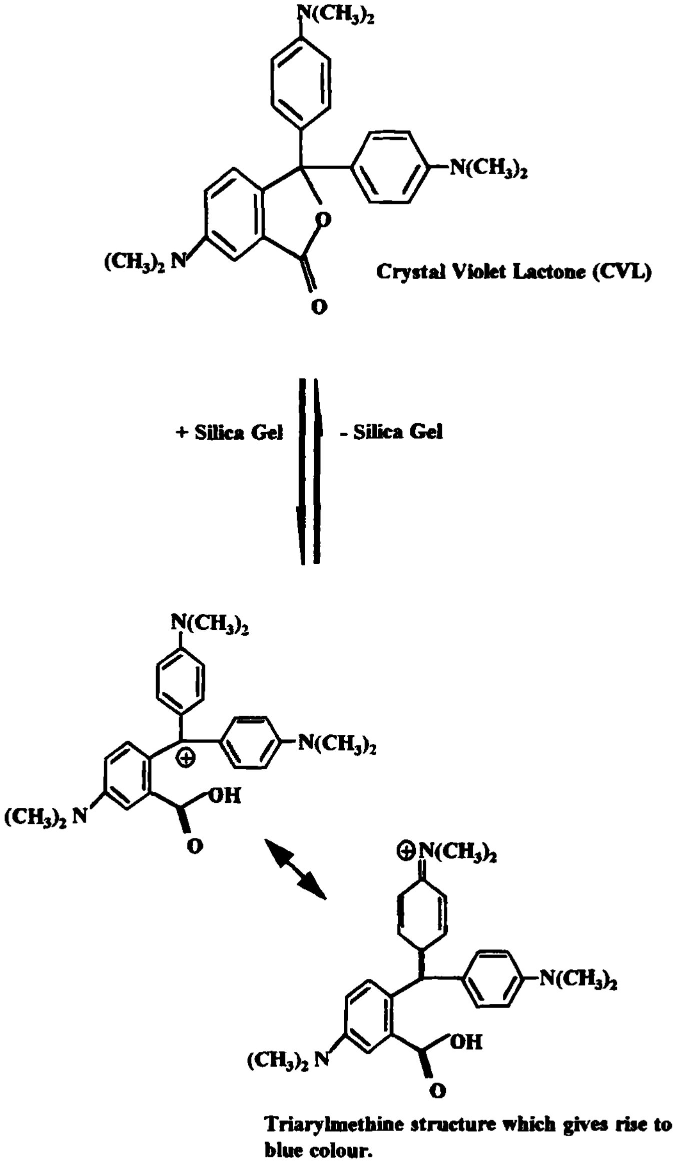

FIG. 2—*Mechanism of color formation in the CVL/silica gel reaction.*

large amount of compounds eluted up to 5 min. These correspond to the polynuclear hydrocarbons of the diesel oil which interfered with efforts to determine marker and dye in heavy fuel oil. So without an elaborate clean up procedure HPLC is unsuitable in this instance.

Results and Discussion

Crystal violet lactone is a pale yellow powder and when added to fuels such as diesel oil or petrol no color change is observed. CVL has the unique characteristic of being colorless, or nearly so, under normal conditions but changes to an intense blue upon being placed in adsorption contact with highly polar substances such as clay, silicon dioxide or when in contact with weak acids [2].

Thus when silica gel is added to fuel containing CVL the silica gel turns a blue color.

This color is generated by the lactone binding to the silica gel and causing ring opening to occur (Fig. 2) and the blue colored triarylmethine formed. This color change is the basis for the use of CVL in carbonless copy paper where CVL and acids are microencapsulated and the pressure of writing causes the capsules to break and the reaction to occur [*3*–*5*].

Its use as a marker was considered because it dissolves readily in diesel oil and it does not color the diesel oil, (which might alert the suspect). It does not interfere with the performance of the engine and it is not a component of diesel oil. Its presence can be instantly detected by the addition of silica gel, confirmed by TLC and quantified by UV

In one case a driver of a truck for a large company was found to be using more diesel oil than expected. Comparison of the service record, itinerary and driving patterns of the truck with other similar trucks on the fleet did not reveal any explanation for the increased consumption of fuel. CVL was added to the bulk tank from which the truck was being fuelled. Subsequent testing of the drivers private vehicle showed it to contain 90% marked diesel oil.

Conclusion

Crystal violet lactone has proved to be a useful marker for detecting larceny of fuel. It can be easily visualized in the field and can be easily analyzed in the laboratory.

References

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