CPRC

CANADIAN POLICE RESEARCH CENTRE

CCRP

CENTRE CANADIEN DE RECHERCHES POLICIERES

TM-I3-95
DEVELOPMENT OF A NEW EUROPIUM BASED FLUORESCENT DYE

By: **Dr. Della Wilkinson**

TECHNICAL MEMORANDUM

Submitted by
RCMP Forensic Identification
Research & Review Section

May, 1995

NOTE: **Further information about this report can be obtained by calling the CPRC information number (613) 998-6343**

EXECUTIVE SUMMARY

This report addresses work covered during the fiscal year 1994/95. Dr. Wilkinson has been researching this area for a while, and has produced other reports which can be read in conjunction with this one.

This report addresses research in the development of a new Europium based fluorescent dye,

experiments - fingerprints on porous surfaces,
experiments - fingerprints on plastics,
future research.

SOMMAIRE

Le present rapport porte sur les recherches menées par le professeur Wilkinson au cours de l'exercice 1994-l 995. Comme ses travaux portent sur ce domaine depuis longtemps, il est possible de consulter ses autres rapports en même temps que celui-ci.

Sujet de recherche:

Creation d'un colorant fluorescent à base d'europium

essais : revelation d'empreintes digitales sur des surfaces poreuses
essais : revelation d'empreintes digitales sur des matières plastiques
recherches futures

The research described in this report was conducted fulltime from April 1994 to September 1994 and then on a part-time basis from January to March 1995 under contract to the Royal Canadian Mounted Police (RCMP). Progress has been made in the area stated within the contract that describes work done upon request by the Field Identification Research and Review Section of the RCMP.

Development of a New Europium Based Fluorescent Dye

Summary

Chemical modification of TEC (Final Report 1992/93) by the addition of two bulky molecules of a chemical called tri-octyl phosphine oxide (TOPO) resulted in good transfer characteristics of the dye into lipid prints on porous surfaces. Much time has been spent on investigating techniques that reduce the quantity of fluorescent dye in the background. Some success has been made with the use of competing chelates that react with the europium ion to form non-fluorescent chelation compounds.

The testing of this new solution on plastic surfaces was identified in the final report 1993/94 and may provide an alternative visualisation technique for use on cocaine exhibits which are notoriously difficult to treat with existing techniques. This testing lead to the replacement of the synergic group TOPO with the less bulky synergic group tri-butyl phosphine oxide (TBPO) which lead to a dramatic improvement in background and thus contrast. The use of surfactants to wash the treated articles after exposure to the TECTBPO solution has also shown encouraging results.

Introduction

From previous research (Final Report 1993/94) into this topic we know that transfer of europium chelates into the lipid component of fingerprints is possible but that the current approach of using a two phase system to promote transfer needs fine tuning to be really effective on porous surfaces. The main problem appears to be one of solubility of the very bulky TECTOPO molecule which deposits onto the background surface. TECTOPO is produced according to equation (1). Two strategies have been selected to solve this problem; the first involves modification of this material to improve solubility; and, the second requires the development of methods for removing any fluorescent material that does deposit on the background.

$$EuCl_3.6H_2O + 3TTA \text{ -t } 2TOP0 \qquad Eu(TTA)_3.2TOPO \qquad (1)$$

This section of the report naturally falls into two categories; 1) the recovery of fingerprints on porous surfaces; and, 2) the recovery of fingerprints on plastic surfaces.

Experiments: Fingerprints on Porous Surfaces

Wash Solutions containing Competing Chelates

Europium ions will chelate with molecules other than thenoyl tri-fluoroacetone (TTA) to produce chelation complexes that are not fluorescent under ultraviolet excitation. The objective is to identify suitable competing chelates that will chelate with the europium found in the fluorescent TECTOPO deposited on the background to produce a non-fluorescent chelate. The TECTOPO held within the lipid print will be protected because the wash solution will be aqueous which prevents penetration into the hydrophobic lipid. To date experiments have been conducted on citric acid, the disodium salt of EDTA and the calcium salt of acetic acid. It appears that concentrations of these materials must be carefully controlled to avoid damage to the print. This is one area that requires more research.

Detection of aged fingerprints

TECTOPO (0.1 g/l in 70% methanol) is extremely good at detecting fresh prints deposited on paper products (xerox and lined papers). The ability of the dye to visualize aged prints is of great importance. Fingerprints were deposited on xerox and lined paper samples which were cut in half. One half was treated immediately with TECTOPO solution the other halved samples were left for varying periods of time to a maximum of five days. They were then treated in the same manner as the fresh samples before being compared. The current TECTOPO solution appears to be effective on prints that are up to three days old.

Comparison to Physical Developer using Depletion Prints

The sensitivity of TECTOPO solution was tested on samples of depletion prints. Donors were asked to deposit prints from one finger only and to deposit at least ten latents in sequence. These samples were exposed to the solution for five minutes and the number of prints visualised was counted. For comparison purposes the experiment was repeated except samples were cut in half with one half being treated with TECTOPO and the other half being treated with physical developer. Experiments are being conducted to compare the sensitivity of TECTOPO to physical developer with aged fingerprints.

Experiments: Fingerprints on Plastics

New Solvent Combinations for TECTOPO

Different solvent systems were identified on the basis of their boiling points, miscibility with water and each other, and their ability to dissolve lipids. Out of eight organic solvents chosen for their physical properties including their ability to dissolve TECTOPO, four showed excellent transfer into the prints and little background contamination when tested on fingerprints deposited on foil. These

solvents were ethyl acetate, acetone, ethanol and methanol. When tested further on black plastic and clear plastic only the methanol and acetone solutions showed promise and were tested on grocery bags. Both of these solutions resulted in significant levels of TECTOPO on the background which reduced the contrast although still visualised the print. This has been a consistent problem with paper and non-porous surfaces but we hope that with the use of a wash solution containing competing chelates the TECTOPO that does deposit on the background surface can be "cleaned up". To date the most promising solvent combination for the visualisation of fingerprints on plastics is 70% methanol in water.

Comparison of TECTOPO with Existing Techniques

An experiment to compare TECTOPO to existing treatments for visualising fingerprints on plastics was completed. Prints on several non-porous surfaces including a wide selection of plastic bags and Styrofoam, were developed using small particle reagent, cyanoacrylate/TEC dye, and, TECTOPO. For fresh prints TECTOPO was excellent even giving clear ridge detail on Styrofoam, however, on aged prints (5 days) CA/TEC was the most impressive technique.

Replacement of TOPO with TRPO

The replacement of the synergic reagent TOPO (8-carbon chain) with TBPO (4-carbon chain) was very successful producing a more soluble europium chelate. Experiments showed excellent transfer of this new material into fingerprints with decreased background fluorescence being observed.

Effect of pH variation on Transfer of TECTBPO

Fluorescence emission spectra were recorded for TECTBPO over the pH range 4 to 9. The intensity of fluorescence output at 614 nm increased from pH 4 to 8 where it peaked, then dramatically decreased for pH 9. This trend was also observed for TEC. Although the solution fluorescence is significantly influenced by pH changes when the dye is absorbed onto the print the pH does not appear to drastically alter the brightness of the print. The buffer appears to inhibit transfer into the lipid print which may be a consequence of its effect on the partition ratio of TECTOPO between the methanol in the lipid and the methanol in the aqueous solution.

Determination of a TECTOPO Working Solution

The solubility of TECTBPO was found to be 4 grams per litre of 70% methanol in water. An experiment to observe the effect of varying the TECTBPO concentration on the transfer of the fluor into lipid prints deposited onto plastics was completed. A 4.0 g/l solution in 70% MeOH gave the brightest best contrasting prints. The resultant prints are comparable in brightness to CA/TEC prints. No deterioration of detail noted after several days.

Different Wash Solutions

Several aqueous wash solutions were tested (methanol, surfactant and citric acid). Pre-washing samples with anionic surfactant proved ineffective at removing TECTOPO from the background, however, washing after dye-ing with TECTBPO was extremely successful at removing the background without damaging the print detail. No significant improvement in background could be observed when treated surfaces were washed with citric acid or methanol since print quality also deteriorated as was observed for TECTOPO prints. Washing with aqueous tergitol-7 (1 ml/l) appears to be an ideal initial wash when followed by gentle rinsing with a stream of water.

Lifetime of Solution

The ability of aged solutions to detect prints was observed. To date a six week old solution continues to visualize bright prints with good background clearance of the dye.

Discussion

A working system has been successfully developed that is capable of visualising fingerprints on paper. The fingerprints all show excellent continuous ridge detail that is brightly fluorescent. The current recommended solution contains 0.1 g/l TECTOPO in 70% MeOH (no buffer). The drawbacks with this technique at present are that most inks will run as a consequence of the solvents used and that the solutions have only been thoroughly tested on fresh prints.

As for the application of this technique to cocaine exhibits we are waiting for the results of the field study.

Future Research

1. **Older samples need to be tested to confirm that the solution does not just work on freshly deposited prints.**
2. **Work needs to be done to determine if TECTOPO treatment can be used sequentially after ninhydrin or DFO.**
3. **Finally a series of comparison tests of TECTOPO to all the current fingerprint treatments available for porous surfaces.**