FORENSIC CONTACT TRACE CHARACTERIZATION

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CONTENTS

(I) Introduction

The research reported in the following papers is mainly concerned with the application of luminescence and chromatographic techniques to the characterization of contact traces in forensic science: for example, for the establishment of evidence that a material transfer has or has not occurred between a suspect and a scene of crime.

There is no originality simply in this application. Luminescence and chromatographic techniques have been applied in forensic work for very many years. But the recent advances in the technology of chemical instrumentation have greatly increased the power of these techniques, along with many others. Hence the tools are now readily available with which the various phenomena made use of in forensic work may be studied and our understanding of them advanced far beyond the old empiricism.

An attempt at understanding may be justified, subjectively, in its own right. But apart from this: without understanding, evidence cannot be competently given, and new techniques, new applications and new types of evidence cannot arise, and progress will cease. Forensic science would be reduced to a charlatanism.

For new knowledge to develop, any area of science must greatly depend on ideas and technology developed outside itself. But this must be a two-way process, each area interacting and contributing to another. Forensic science too must profit from and contribute to this process. It is hoped that at least in the foregoing respects these papers will play a part.

(II) Summary and Commentary

SYNCHRONOUS LUMINESCENCE AND RELATED TOPICS

Papers 1-17

Many contact traces are luminescent. Often the nature of their luminescence is poorly understood; often highly complex mixtures are present, which conventional techniques cannot resolve. The synchronous excitation technique, developed in this research, has greatly advanced the resolution obtainable and our understanding of these mixtures. It also provides fluorescence fingerprints that may be taken as evidence of a common origin, or otherwise, of different samples of material (1,2).

The early work was much concerned with developing our knowledge of the nature of the luminescence of mineral oil lubricants, which occurred regularly as contact traces that could be characterized only very poorly at that time. This work resulted in the identification of over forty different fluorescences, most of which were produced during usage of an oil and were previously of unknown occurrence in much of the material examined (4). Examples were given of the technique's application in providing spectral fingerprints, and the first case work results were reported (3). Other materials investigated included petroleum fuels, greases, soots, bitumens, and coal-derived products (3,4).

Under some circumstances it was found that further spectral detail could be obtained from partially quenched spectra (5), which was exploited when the striking effect of fluorescent tyre print formation was discovered during a scenes-of-crime search (6). The phenomenom and the circumstances favouring its occurrence and observation were investigated in detail (7) and, hence, new spectrometric techniques for the characterization of rubber contact traces were introduced. Other papers largely concerned with tyre print formation were published (9,10) that included further results of work on the formation and the visual detection of the prints; and a brief publication giving various examples of luminescence applications in forensic science appeared (8).

At this stage the synchronous technique lacked an adequate basis on which the spectra it produced could be understood and predicted from the luminescence characteristics of any compound of interest. An ability to make such a prediction is important, for example, to the optimization of experimental parameters in whatever application of the technique is being made. A theoretical basis was therefore developed and the derived equations reduced to a readily used form that gave excellent results when applied to a considerable variety of compounds (11).

As in any other technique the effective application of luminescence spectrometry depends on a sufficient understanding of its pitfalls, and of how they may be dealt with. The most important of these remains the inner-filter effect. There are many examples in the literature where work has been rendered of highly questionable significance, if not invalidated, by the effect. One example involves the published polemic (13) with the Winefordner group; and another, the correct choice of experimental conditions for the detection of certain fatty acid derivatives in high performance liquid chromatography (29). Furthermore, no standardization of methods between laboratories is possible unless the effect is always taken into account. It is hoped that a more widespread recognition of the effect and of the appropriate countermeasures will be promoted by the recently published review (16).

Another problem of practical significance is the lack, commercially, of solvents of satisfactory purity for forensic work, and trace work generally. This arises partly because of the inadequate nature of some of the standards used or of the ways in which they are applied. A new criterion for solvent purity was introduced, based on synchronous Raman bands (12), which could provide a remedy. Interest in this has since been indicated by some manufacturers.

The earlier work both in this and in other laboratories on the analysis of mineral oil traces was subject to the limitations imposed by the use of uncorrected spectrometers. Thus, spectral comparisons could not be made between results produced from different spectrometers, or from one spectrometer over an extended period of time. Since the original work, corrected spectrometers have become commercially readily available. It was feasible, therefore, to develop well-standardized methods, based on the earlier work and on the knowledge gained since (14), that would be appropriate to the establishment of a data collection from petroleum products so that evidential significance might be more readily placed on a numerical basis. The results of this work on a file of data based mainly on case work samples has now been reported (15).

Apart from the materials already mentioned, luminescence techniques have been applied to many others in case work, with valuable results. The list of materials is extensive and includes candle waxes, cosmetics, fire debris, foodstuffs, some types of paint, fibres, plastics, resins, detergent products, liquor stains, inks, fluorescent markers, soils, water, trace metals and cyanide in water, match heads, carcinogens in various materials, and toxicological samples. A regular requirement has been the identification of faecal traces, for which earlier techniques had proved insensitive and unreliable. The synchronous luminescence technique that was developed is now in print (17) and finds frequent application.

As well as its usage in forensic science laboratories, the synchronous luminescence technique has been taken up and applied in many other areas, as was originally predicted (1,2). Examples given in the literature by other workers include the analysis of industrial effluents for polynuclear hydrocarbons and heterocycles, and for other toxic materials, phenols in waste water, hydrological tracers, crude oils, fuel oils, oil spill samples, lacustrine sediments, marine sediments and sea water, various environmental contaminants, phosphorimetric analysis of coal-derived materials, drugs, cigarette smoke, amino acids, proteins, and the binding of a carcinogen to nucleic acids.

The technique is now a standard provision on commercial spectrometers generally. One organization has included it within the facilities of a mobile laboratory used for emergency environmental work.

LUMINESCENCE FROM SURFACES

Papers 18-22

Luminescence from solid surfaces is of frequent interest in forensic science, in the search for contact traces, for example, and in other areas of analytical chemistry, such as thin layer chromatography detection techniques.

A study was made of the fluorescence of adsorbates on silica gel (18), in which the transfer of a proton from the adsorbent to an excited state adsorbate was discovered. This lead to a microcolumn liquid chromatography technique and to the introduction to high performance liquid chromatography (h.p.l.c.) of a new technique, based on a packed flow-cell, which has been widely used and reported since by other workers for the analysis of aflatoxins. An application in the field of indole alkaloids has also been reported. For some of the former class of compounds the detector has been recommended for adoption in an official method of analysis, and packed flow-cells are now articles of commerce.

A development of this work adapted the room temperature phosphorescence of adsorbates on dry cellulose to a flow-cell technique, by which the necessity for the presence of water for the formation of a subsequently phosphorescent adsorbate was discovered (19). The room temperature phosphorescence effect, for which some previously unrecognized references were reported (20), has now been used for marking fluorescent cellulose surfaces (22).

The surface fluorescence of glass was studied, and a technique developed for the differentiation of float (tin-containing) from non-float surfaces on very small fragments of glass. The potential effect of this is to virtually double the evidential significance of one of the most commonly encountered materials in forensic science (21).

CHROMATOGRAPHIC WORK

Papers 4,18,23-31

Some aspects of this have been mentioned already under papers 4 and 18. These include probably the first report of a microcolumn h.p.l.c. experiment (18).

A thin layer chromatography (t.l.c.) technique was developed for the detection of traces (down to 5 ng in recent usage with modern materials) of some explosives components, which has since made a vital contribution both in this and in many other laboratories to the investigation of bombings and other explosives offences, and to the examination of swabs taken from suspects (23). In some other t.l.c. work (28) fluorescent brighteners were characterized in microgram amounts of fibre.

Research on the use of fluorescence derivatization in h.p.l.c. has emphasized a number of important factors that have previously been overlooked (29). This lead to the development of a new series of derivatives that enabled fatty acids to be detected down to the femtogram level (30). Since its publication this development has been of particular value, in forensic science work, to the detection and identification of fats; for example, the demonstration of the presence of human fat on a vehicle alleged to have been involved in a fatal accident, and the non-human origin of fat present on a knife thought to have been used in a case of murder.

Other papers under this heading are concerned with gas chromatography (g.c.) work (24-27,31), particularly in connection with capillary column and pyrolysis techniques, and include some of the first published examples of a coupling of the two (26). The recent application of capillary g.c. to mineral oil lubricants (31) should further the evidential significance of such materials.

MISCELLANEOUS

Papers 32,33

This includes an early technique for the comparison of the density of glass fragments (32), which found much case work application at the time; and a technique for the separation from brake fluids of mineral oils for analysis by some of the earlier mentioned techniques (33).

(III) List of Publications

The submitted publications are listed below under subject headings. These are, however, to some extent arbitrary as there is considerable overlap between the classifications. For example, the paper on silica gel adsorbate fluorescence (18) could equally well be included under the chromatography classification. Within each classification the papers are listed chronologically.

SYNCHRONOUS LUMINESCENCE AND RELATED TOPICS

1. "Synchronized Excitation of Fluorescence Emission Spectra"
   Nature, Physical Science, 1971, 231 (20), 64-65.

2. "The Nature and the Evidential Value of the Luminescence of Automobile Engine Oils and Related Materials. Part I. Synchronous Excitation of Fluorescence Emission"
   J. Forensic Science Society, 1971, 11 (2), 83-94.

3. "The Nature and the Evidential Value of the Luminescence of Automobile Engine Oils and Related Materials. Part II. Aggregate Luminescence"
   J. Forensic Science Society, 1971, 11 (3), 153-170.

4. "The Nature and the Evidential Value of the Luminescence of Automobile Engine Oils and Related Materials. Part III. Separated Luminescence"
   J. Forensic Science Society, 1971, 11 (4), 235-253.

5. "Partly Quenched, Synchronously Excited Fluorescence Emission Spectra in the Characterisation of Complex Mixtures"
Analyst, 1974, 99 (11), 729-738.

6. "Murder Involving Discovery and First Application of Fluorescence of Tyre Prints"
Nature, 1974, 250 (5469), 762-764. (With J. H. Loughran and T. R. Watson)

7. "Characterisation of Rubbers, Rubber Contact Traces and Tyre Prints by Fluorescence Spectroscopy"
Analyst, 1975, 100 (2), 82-95.

8. "Spectrophotofluorimetry and -phosphorimetry [in Forensic Science]"
Chemistry in Britain, 1975, 11 (12), 442-443.

9. "Luminescence of Tyre Marks and Other Rubber Contact Traces"
J. Forensic Science Society, 1976, 16 (1), 5-19.

10. "Make the Traces Glow"
Industrial Research, 1977, Nov. 15th, 29-32. Also in Spectrum, 1976, (145), 2-5; Elektor, 1977, 3 (3), 12-15

11. "Prediction of Peak Wavelengths and Intensities in Synchronously Excited Fluorescence Emission Spectra"
Analytical Chemistry, 1977, 49 (12), 1710-1715. (With I. W. Evett)

12. "Raman Peaks in Synchronously Excited Emission Spectra as a Reference for Purity of Fluorescence-grade Solvents"
Analyst, 1977, 102 (10), 782-785.

13. "Exchange of Comments: Limitations of Synchronous Luminescence Spectrometry in Multicomponent Analysis"
Analytical Chemistry, 1980, 52 (1), 189-191.

14. "Examination of Petroleum Products of High Relative Molecular Mass for Forensic Purposes by Synchronous Fluorescence Spectroscopy. Part I. Appraisal of Experimental Factors"
Analyst, 1980, 105 (2), 97-109.

15. "Examination of Petroleum Products of High Relative Molecular Mass for Forensic Purposes by Synchronous Fluorescence Spectroscopy. Part II. Discrimination Within an Arbitrary Set of Representative Samples.
J. Forensic Sciences, 1980, 25 (3), 589-602. (With I. W. Evett and J. M. Dubery)

16. "Inner Filter Effects, Sample Cells and their Geometry in Fluorescence Spectrometry"
Standards in Fluorescence Spectrometry, edited by J. N. Miller for the UV Spectrometry Group, Chapman and Hall, 1981, 27-43.

17. "A Spectrometric Study of the Fluorescence Detection of Fecal Urobilinoids"
J. Forensic Sciences, 1982, 27 (2), 352-365.

LUMINESCENCE FROM SURFACES

18. "Nitrogen Heterocycle and Polynuclear Hydrocarbon Fluorescence and Adsorption Effects in the Presence of Silica Gel. Applications in High-pressure Liquid and Microcolumn Chromatography"
    Analyst, 1975, **100** (8), 529-539.

19. "Packed Flow-through Cell Technique for the Measurement of the Room-temperature Phosphorescence Spectra of Adsorbed Compounds"
    Analyst, 1978, **103** (7), 775-776.

20. "Phosphorescence of Adsorbed Molecules at Room Temperature - The First Observations?"
    Talanta, 1979, **26** (2), 180. (With J. N. Miller)

21. "Fluorescence Spectrometry in the Identification and Discrimination of Float and Other Surfaces on Window Glasses"
    J. Forensic Sciences, 1981, **26** (2), 325-342.

22. "Room Temperature Phosphorescence Marking of Fluorescent Cellulose Surfaces with Adsorbed Organic Phosphors"
    J. Forensic Science Society, 1982, **22** (2), 161-164.

CHROMATOGRAPHIC WORK

23. "Detection of Microgram Amounts of Nitroglycerin and Related Compounds"
    J. Forensic Science Society, 1967, **7** (4), 198.

24. "Additive Group Retention Indices in Gas Chromatography"
Analyst, 1972, 97 (9), 708-709.

25. "Gas Chromatographic Characterization of Cooking Fats with Reference to a Case of Murder"
J. Chromatography, 1973, 77, 228-232. (With B. R. G. Roberts)

26. "Some Applications of a Capillary Column Gas Chromatography System in Forensic Science"
Scan, 1973, 3 (3), 13-15. (With K. Hadley)

27. "Pyrolysis Gas Chromatography over Hydrogenated Graphitized Carbon Black. Differentiation of Chewing Gum Bases for Forensic Purposes"
J. Chromatography, 1974, 101, 417-423. (With K. Hadley and B. R. G. Roberts)

28. "Forensic Significance of Fluorescent Brighteners: Their Qualitative TLC Characterisation in Small Quantities of Fibre and Detergents"
J. Forensic Science Society, 1977, 17 (2,3), 145-152.

29. "Fatty Acid Esters of 4-Hydroxymethyl-7-methoxycoumarin: Fluorescence Characteristics and their Variation in High Performance Liquid Chromatographic Solvents"
J. Chromatography, 1979, 178, 249-258.

30. "Phenanthrimidazoles as Fluorescent Derivatives in the Analysis of Fatty Acids by High Performance Liquid Chromatography"
J. Chromatography, 1980, 189, 359-373.

31. "Capillary Column Gas Chromatography in the Examination of High Relative Molecular Mass Petroleum Products"
J. Forensic Science Society, 1982, 22 (3), 283-287.

MISCELLANEOUS

32. "A Simple Density Gradient Technique for the Comparison of Glass Fragments"
J. Forensic Science Society, 1969, 9 (3,4), 115-117.

33. "A Note on the Detection and Determination of Mineral Oil Contamination in Brake Fluids"
J. Forensic Science Society, 1982, 22 (3), 289-290.

The above material has provided the basis of lectures to the Chemical Society, the Society of Analytical Chemistry, the Institute of Physics, the Forensic Science Society, and of a BBC broadcast interview. On occasions press reports have appeared in the 'Times', the 'Guardian', the 'Financial Times', the 'Wall Street Journal', 'Chemical and Engineering News', and others.