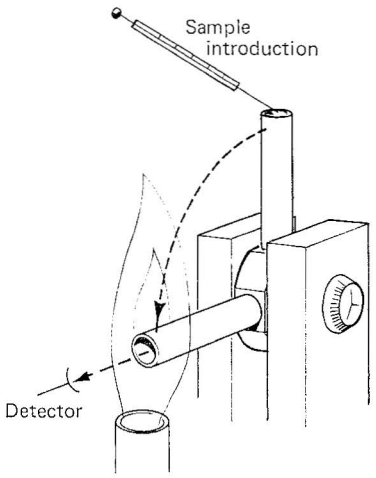

Fig. 9. MECA sample-introduction system.

in coal: organic, pyritic and sulphate sulphur. The method shows some promise for this purpose and the results can be obtained in a few minutes. Sulphur can also be determined in iron ore, pitch, pharmaceutical products, lichens, teeth, etc.

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Forensic Analysis

The following are summaries of four of the papers presented at a Meeting of the Analytical Division held on November 5th, 1975.

Forensic Applications of Liquid Chromatography

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High-pressure liquid chromatography (HPLC) was first used in the Metropolitan Police Laboratory in 1971. At that time, a broad-based research programme was initiated to cover column packing techniques, methods of preparing packing materials, detector design and injection systems as well as applications. As a result of this work, HPLC is now in routine use for a number of forensically important analyses.

Although a variety of detectors are available for HPLC, there is no detector that is capable of universally detecting 0.1–10-ng amounts of compounds in eluates. In the forensic field, where samples are often very small, detector sensitivity imposes a severe limitation on the areas of application. In our work we use only ultraviolet absorption and fluorimetric detectors.

This has enabled methods of adequate sensitivity to be developed for drug samples, where milligram amounts or more of illicit preparations are often available for analysis, but has allowed smaller samples to be analysed only if the components display fluorescence.

During the period in which HPLC has been in use there has been a tendency for the particle size of the packing materials used to be reduced, because this reduction leads to improved chromatographic efficiency. The theoretical basis for this procedure has been described elsewhere[1] and its practical significance in reducing peak broadening is shown in Fig. 1. All columns currently used for routine analysis are packed in the laboratory with materials in the 5–10-μm size range. The packings are either silica or silica chemically modified with octadecyltrichlorosilane.[2,3]

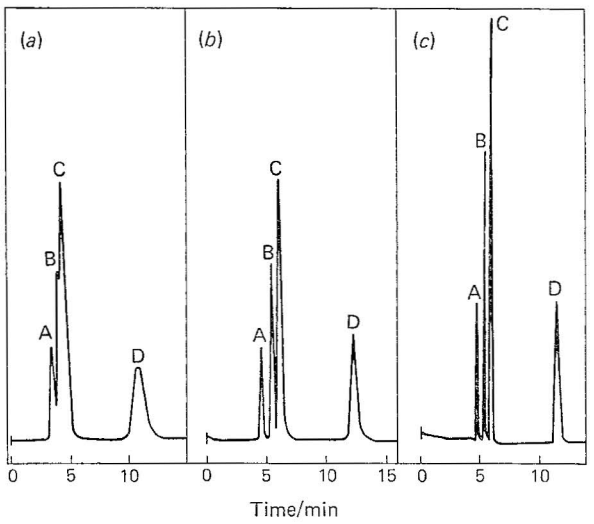

Fig. 1. Influence of particle size on column efficiency. A standard mixture of (A) toluene, (B) biphenyl, (C) phenanthrene and (D) nitrobenzene separated on three columns of identical dimensions packed with silica gel of different particle size (prepared by sedimenting a thin-layer chromatography silica). Column: 25 cm × 4.9 mm i.d., packed with silica of particle size (*a*) 40–50, (*b*) 10–20 or (*c*) 5–10 μm. Solvent: isooctane saturated with acetonitrile. Flow-rate: 1 ml min^{-1}. Pressure drop: (*a*) 40; (*b*) 375; and (*c*) 750 p.s.i. Detector: ultraviolet at 254 nm.

Applications

Cannabis Comparison

HPLC using reverse-phase chromatography affords one of the best ways of comparing cannabis samples.[2] Typical chromatograms are shown in Fig. 2 and it has been established that the major peaks being displayed are due to neutral and acidic cannabinoids.[4]

Screening of Illicit Drug Preparations

Many illicit drug preparations are encountered in the work of this Laboratory and their analysis is usually based on a combination of extractive, spectroscopic and chromatographic methods. Many of these illicit preparations contain basic drugs and in such instances HPLC on silica columns using methanol - aqueous buffer mixtures permits rapid screening of samples in qualitative and quantitative modes.[5]

LSD

The usual way in which lysergic acid diethylamide (LSD) is encountered is in the form of the so-called micro-dots, *i.e.*, small tablets containing up to 100 μg of the active hallucinogen. The presence of LSD in such preparations can be rapidly established by crushing the sample in methanol and injecting an aliquot of the extract on to an HPLC column. Using methanol - 0.2% ammonium carbonate (or 0.2 M ammonium nitrate) (3 + 2) as eluting solvent, it is possible to separate LSD rapidly from related ergot alkaloids on a silica column (see Fig. 3).

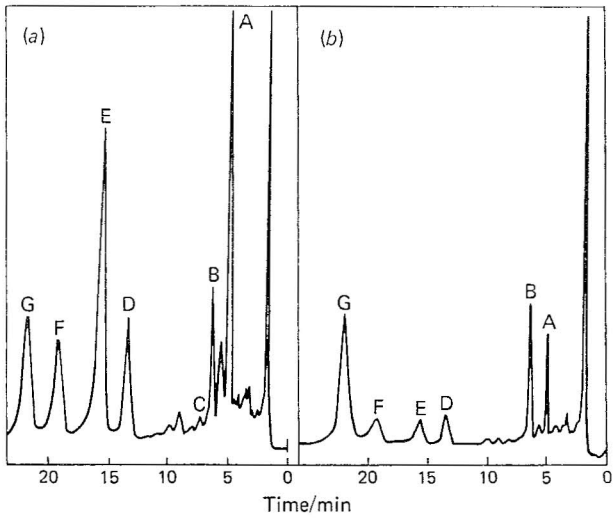

Fig. 2. Liquid chromatograms of cannabis extracts from two different resin samples. The peaks correspond to: (A) cannabidiolic acid; (B) cannabinol; (C) Δ^9-tetrahydrocannabinol; (D) cannabinolic acid; (E) Δ^9-tetrahydrocannabinolic acid; (F) cannabichromenic acid; and (G) internal standard. Column: 25 cm × 4.9 mm i.d. packed with Partisil 5 modified with octadecyltrichlorosilane. Solvent: methanol - 0.02 N sulphuric acid (4 + 1). Flow-rate: 2 ml min^{-1}. Pressure drop: 3 000 p.s.i. Detector: ultraviolet at 254 nm.

Using fluorimetric detection, it is possible to detect LSD selectively down to low levels. This selectivity has advantages for the analysis of tablet extracts containing ultraviolet-absorbing co-extractives, and the sensitivity has been put to the test in detecting LSD in urine extracts.

Chinese heroin

This material is a mixture of heroin and caffeine together with a number of other minor constituents. HPLC on a silica column with methanol - 2 M ammonia - 1 M ammonium nitrate (27 + 2 + 1) enables the major constituents of the mixture to be separated.[5] The chromatogram can be used to provide quantitative information.

Phenylethylamines

Illicit preparations containing amphetamine and related drugs are often submitted for analysis. Although the components of such mixtures can be separated by gas chromatography on alkali-treated columns, HPLC affords a more rapid and trouble-free analytical screening procedure. The relative proportions of the various components in such mixtures can be readily deduced from the liquid chromatograms and have value in providing "drugs intelligence" information, as the composition of illicitly prepared materials will often show considerable variation from batch to batch (see Fig. 4).

Opium comparison

Raw opium samples display variations in the proportions of the alkaloids that they contain. Separations on a silica HPLC column using the same solvent system as used for Chinese heroin enables samples to be readily compared.

Separations of Mixtures Containing Polynuclear Hydrocarbons

Polynuclear hydrocarbons can be very readily separated by reverse-phase HPLC.[3] In addition to having strong ultraviolet absorbance, these compounds also have fluorescence properties, which can be exploited in their detection. Flow cells have been made that enable a commercial fluorimeter to be converted into an HPLC detector,[6] and a sensitive laboratory-made detector has also been constructed.[3] HPLC in combination with ultraviolet and/or fluorimetric detection has been used to study the variation in the polynuclear hydrocarbon content of several different types of sample.

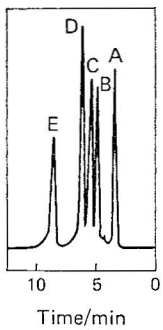

Fig. 3. Liquid-chromatographic separation of LSD and related compounds. Column: 25 cm × 4.9 mm i.d. packed with Partisil 5. Solvent: methanol - 0.2% ammonium carbonate (3 + 2). Flow-rate: 1 ml min^{-1}. Pressure drop: 1 400 p.s.i. Detector: fluorimetric, excitation 320 nm, emission 420 nm. Components: (A) lysergic acid, (B) lysergamide; (C) LSD; (D) lysergol; and (E) iso-LSD.

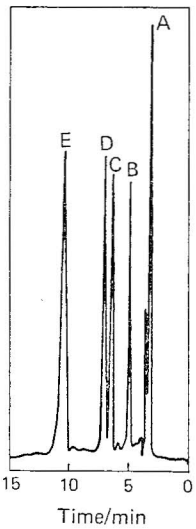

Fig. 4. Liquid-chromatographic separation of compounds found in illicit amphetamine preparations. Column: 25 cm × 4.9 mm i.d. packed with Partisil 5. Solvent: methanol - 2 M ammonia solution - 1 M ammonium nitrate (27 + 2 + 1). Flow-rate: 1 ml min^{-1}. Pressure drop: 1 500 p.s.i. Detector: ultraviolet at 254 nm. Components: (A) benzphetamine; (B) amphetamine; (C) ephedrine; (D) methylamphetamine; and (E) atropine.

Used engine oils

Polynuclear hydrocarbons build up in engine oils during use,[7] and such oils, when injected on to an octadecyltrichlorosilane-modified silica,[3] yield complex chromatograms that can be used as "fingerprints." Chromatograms of oils from different vehicles, or from the same vehicle after different degrees of use, show differences in the relative proportions of the various polynuclear hydrocarbons that they contain. It is possible to use the technique to compare oil samples taken from the surface at the scene of an incident with drops of oil from a suspect vehicle. Typical chromatograms are shown in Fig. 5.

Bitumen paints

Analytical comparison of paint flakes or smears is a common forensic problem. With bitumens, such comparisons by conventional techniques can often be difficult. In certain bitumens that contain coal tar pitch it is possible to obtain chromatograms from the polynuclear content of the material and these chromatograms can be used for comparison.

Soils

Extracts of organic material from soil yield chromatograms under the same HPLC conditions as those used to separate polynuclear hydrocarbons. It is assumed that some of the fluorescent components observed are derived from particulate matter coming from the atmosphere, and it is possible that a comparison of soil samples could be made on the basis of such chromatograms.

Future Trends

As mentioned earlier, sensitivity is one of the limiting factors that preclude HPLC from being more widely applied in the forensic field. If a compound possesses natural fluorescence, or if this property can be induced by chemical reaction, then under optimum conditions it is often possible to detect as little as 10–100 pg of material in an HPLC eluate. By exploiting

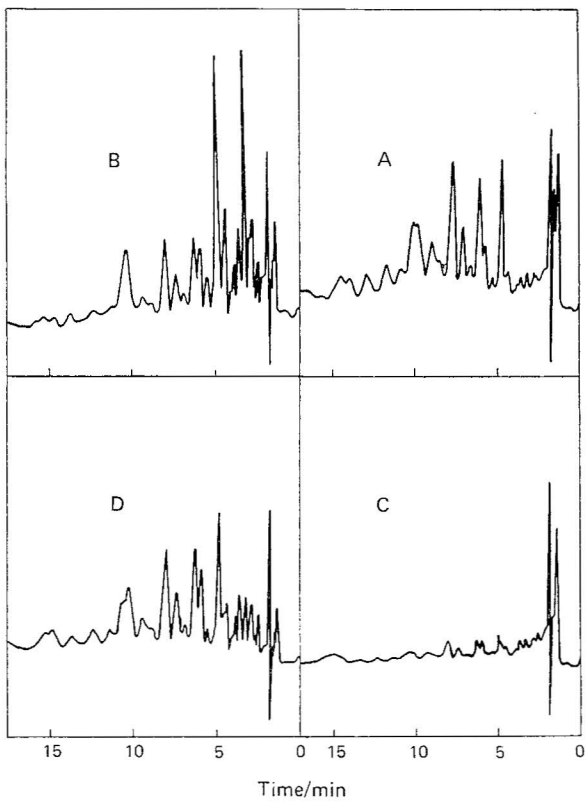

Fig. 5. Liquid chromatograms of used engine oils. The peaks are attributable to polynuclear hydrocarbons present in the four different samples (A–D). Column: 25 cm × 4.9 mm i.d. packed with Partisil 5 modified with octadecyltrichlorosilane. Solvent: methanol - water (9 + 1). Flow-rate: 1 ml min^{-1}. Pressure: 1 000 p.s.i. Detector: ultraviolet at 254 nm.

fluorimetric detection, it should be possible to analyse samples that currently lie outside the scope of HPLC with ultraviolet detection, *e.g.*, detecting low levels of drugs and their metabolites in body fluids, components of paint hydrolysates for paint comparison or metal chelates for the trace analysis of materials such as glass. Work is under way in this area in this Laboratory and a successful method for morphine has already been developed.[8]

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Selective Detectors in Gas Chromatography

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With the advent of gas chromatography (GC) came the problem of the sensitive detection of small amounts of eluate. The successful design of adequately sensitive and stable detectors with wide applicability has been followed by a second phase of detector development aimed at increasing detector selectivity in order to simplify chromatograms of complex mixtures.