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MODIFIED METHOD FOR ANALYSIS OF C_2–C_5 HYDROCARBONS IN AN AROMATIC–ALKANE MATRIX USING AN AUTOMATED THERMAL DESORBER

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SUMMARY

An automated thermal desorber, Model ATD-50 (manufactured by Perkin-Elmer), packed with a Tenax-TA cold trap was used in conjunction with a 50 m × 0.22 mm I.D. fused-silica BP-1 capillary column to separate light hydrocarbons entrained in an aromatic–alkane mixture. Injection of samples was achieved using the standard injection port fitted to the ATD-50. Collection of the material at −30°C on the cold trap preceeded volatilisation and desorption of the trapped volatiles across 1 m of a heated fused-silica transfer line and onto the head of the column. The column oven is held at −35°C, where refocussing of the desorbed materials takes place. The oven is held isothermally for 8.5 min at −35°C before commencing a dual ramp temperature programme to fully separate the mixture. Sharp, near symmetrical component peaks are obtained across a 235°C span. Cooling is achieved using bottled liquid carbon dioxide pumped into the rear of the gas chromatograph oven.

The method overcomes the need for multiple column systems, heartcutting steps or sample splitting for the analysis of light hydrocarbons and liquid mixtures. An added advantage is that users of ATD-50 systems can use the equipment for both adsorbent tube desorption and conventional hypodermic syringe liquid analysis. The method separates some 32 simple components varying in volatility from methane to 1,2,3-trimethylbenzene in less than 30 min.

INTRODUCTION

Chemical, environmental and industrial hygiene analysts in the petroleum and chemical industries have often experienced difficulties when attempting to analyse samples containing components whose boiling points are significantly different, *i.e.* ethane to trimethylbenzenes. Typically, the sample(s) can only be analysed for a particular range of components determined by their boiling points and method of sample injection at the expense of the remaining components. Further attempts at full range analysis by gas chromatography (GC) have included splitting the sample under conditions of reduced or increased temperature and pressure, *e.g.* partial distillation

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and subsequent analysis of the separated fractions by different chromatographic methods.

Amongst the disadvantages encountered using these techniques are the loss or chemical alteration of key components and the error involved in renormalisation steps when attempting to recalculate the total individual component concentrations for the whole sample. Particular difficulties can be encountered when attempting to analyse for ethane (boiling point $-89°C$) and 1,3,5-trimethylbenzene (boiling point 165°C) in the same sample.

Previous approaches to this problem have involved GC techniques designed to elute all C_2–C_4 components as a single sharp peak and optimise on separation of C_{5+} components[1,2]. Assumption-based calculations are then used to quantify the various C_2–C_4 contributions to the single peak area based on supplementary analytical data on related process streams[3]. Alternatively, some analysts have attempted pressure filling gas syringes and injecting an aliquot of this material into a separate GC set up to optimise on separation of the lighter components. Comparison of data from both techniques is then performed to calculate the ratio of C_1, C_2, C_3 and C_4 summed components to C_{5+} summed components[4,5]. These methods have never yielded consistent satisfactory performance in the laboratory.

Recent GC methods for the total analysis of organic materials increasingly employ cryogenic or "cold-trapping" techniques to focus analytes on the GC column[6]. These methods have included (a) standard injections onto GC columns operated at ambient temperature where the column is cool relative to the injector temperature[7]; (b) direct column cold trapping of analytes in gaseous samples[8,9]; (c) refocussing analytes undergoing thermal desorption, either from (i) Tenax-TA adsorbtion tubes used in direct air sampling[10–13], headspace water sampling[14], purge and trap water sampling[15–18], and direct water sampling[19] or (ii) activated charcoal carbon tubes, utilised in the closed loop stripping of aqueous samples[20], and direct air sampling[21].

A variety of cold trapping techniques have been investigated. The most commonly used involve (a) Monitoring the GC column at temperatures significantly below the boiling point of the desired components of interest utilising liquid carbon dioxide or liquid nitrogen, (b) maintaining the front section of the column at cryogenic temperatures, (c) cryotrapping in a section of unpacked or uncoated tubing at the inlet connection to the column, (d) cryotrapping on an uncoated, coiled loop of presilyated capillary glass tubing, of which 25 cm is immersed in liquid nitrogen[20]. This latter technique was not reported as totally successful since breakthrough losses of compounds (boiling points $<70°C$) occurred, and concluded that such volatile organics could not be quantitatively recondensed by simple capillary cold trapping. GC cryogenic techniques are typically compromised by problems involving the collection of large quantities of water vapour, presenting major difficulties for subsequent GC analysis[11]. Such problems include sample losses, absorption effects, side reactions and the cross-contamination of samples.

A straightforward, one-step method was therefore developed utilising existing GC equipment to trap, refocus and separate simple, petroleum-related components of varying volatilities for subsequent complete GC analysis, affording total analysis of volatile materials within the sample.

EXPERIMENTAL

Chemicals

Standards were freshly prepared using analytical-grade purity materials. Gas mixtures and pure gases were blended (Air Products, Bracknell, U.K.) using both gravimetric and volumetric methods, and injected into sealed all-glass vessels (Hampshire Glassware Scientific, Southampton, U.K.). The gas blends were injected into glass vessels filled to achieve zero headspace with individually prepared liquid organic mixtures. (Sigma, Poole, U.K.). Concentration ratios were adjusted in subsequent standards to cover the typical ranges encountered in "plant process" samples. Immediately prior to injection, fresh standards were stored in polystyrene "picnic" boxes lined with dry ice. Individual hypodermic syringes (Scientific Glass Engineering, Milton Keynes, U.K.) were dedicated to each standard in order to minimise cross-contamination effects. Each syringe was previously solvent cleaned and dried in a stream of ultra-pure nitrogen.

Tenax-TA (20 mg), was packed into the ATD-50 cold-trap (Perkin-Elmer, Beaconfield, U.K.) and sealed with silanised glass wool. The Tenax was then pre-conditioned at 250°C, at 20 ml/min carrier gas flow-rate before use.

Instrumentation

The ATD-50 is a multi-functional instrument the principal role of which is for the analysis of organic vapours at very low concentrations (sub-part per million)[22]. Depending upon the adsorbent material selected for the cold-trapping packing, the trap itself can act as a primary trap over a temperature range spanning from −30°C to 250°C for liquid samples directly injected into the injection port. This is a facility in addition to its' role as a secondary trap for adsorbent tubes desorbed via the normal tube desorption sequence. Cooling of the trap is achieved electronically negating the need or dependance on heat exchange or refrigerant fluids. Retention of the sample when the trap is cooled therefore depends on chromatographic factors rather than condensation. Volatile compounds can now be injected using the "single-stage desorption" as they are quickly released or "fired" from the trap when it is heated up to 250°C. The trap is heated at a rate exceeding 1000°C per min to a defined upper limit of 300°C, sending a narrow band of concentrated sample through the fused-silica transfer line to the gas chromatograph.

Deactivated 1 m × 0.22 mm I.D. fused-silica (Chrompack, London, U.K.) was connected and run from the exit point of the cold trap through the heated transfer line jacket and into the rear of the GC oven, a Perkin-Elmer Model 8320. The silica line was then coiled in the oven and connected via a graphite ferrule into a lined stainless-steel union. The exit point of the union is attached in turn to a cradle mounted 50 m × 0.22 mm I.D. BP-1 wall-coated open-tubular fused-silica capillary column, 0.5 μm film thickness (SGE). The end of the column was then inserted into the outer edge of the flame ionisation detector, at 275°C. Both the ATD-50 and the Model 8320 gas chromatograph were linked to a programmable Perkin-Elmer Model LCI-100 computing integrator to yield chromatographic plotting and retention data.

Subambient cooling of the GC oven was achieved by piping copper tubing directly via a pumping valve accessory directly into the rear of the oven from the carbon dioxide cylinder.

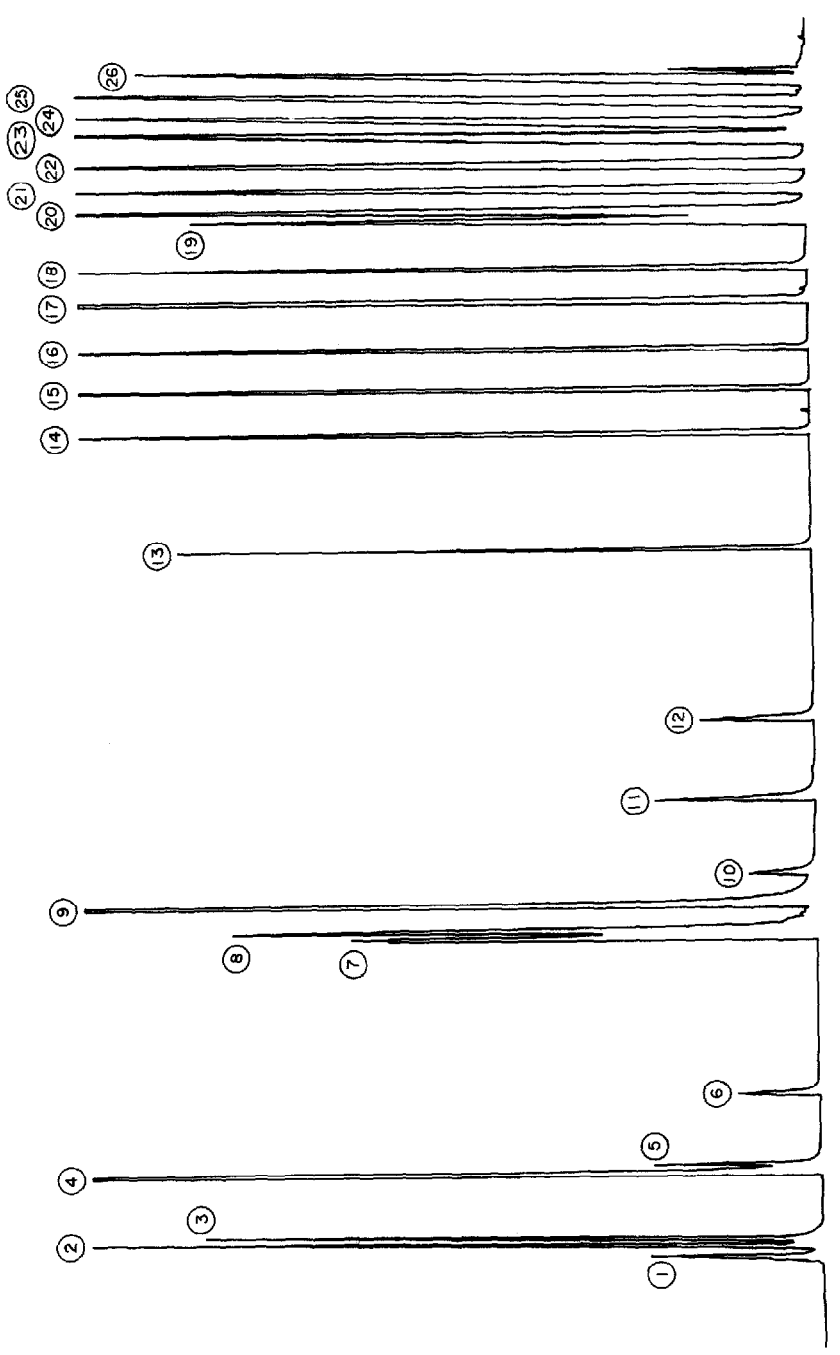

Fig. 1. Chromatogram of calibration standard illustrating the separation of 26 components using the method described in the text. For peak identification see Table I.

System operating parameters. The final selected GC system conditions instituted were as follows. Carrier gas: ultra-pure helium 5.5 grade (Air Products). ATD-50: cold trap packing, 20 mg Tenax-TA; cold trap low temperature, −30°C; cold trap high temperature, 250°C; split ratio (combined), 200:1.

Gas chromatograph. Detector temperature, 275°C; carrier gas flow-rate, 1 ml/min. Temperature conditions. Oven temperature: −35°C; isothermal time 1, 8.5 min; ramp rate 1, 20°C/min; oven temperature 2, 60°C; isothermal time 2, 1.0 min; ramp rate 2, 10°C/min; oven temperature 2, 200°C; final hold time, 1.0 min.

Analytical procedure

Liquid carbon dioxide was pumped into the GC oven until pre-selected cooling temperatures were held and stabilised for a minimum of 3 min. Selected low temperatures were set from −10°C, then decreasing by 5°C steps for each successive GC run down to a minimum start temperature of −50°C. This temperature was determined by experimental observation of the separation performance of the column. Aliquots of the calibration standards varying from 0.4 μl to 0.8 μl were then injected directly into the ATD-50 injection port. Samples were allowed to collect on the cold trap for 15±3 s at −30°C and immediately "fired" into the transfer line.

Upon entering the head of the chilled column, the sample eluates are partially refocussed prior to movement of the chromatographic band down the column. Column flow-rate was measured at 1.0 ml/min. Experiments were then conducted to investigate the low temperature separation of the hydrocarbon components before the column temperature was increased, *i.e.* ramped, in order to separate out the higher boiling materials within a reasonable time profile. Temperature control parameters were recorded and compared with retention and peak area data.

RESULTS AND DISCUSSION

A specimen chromatogram obtained utilising the procedure described in the text is presented in Fig. 1. The peaks are uniformly sharp and exhibit peak widths of less than 6 s at the base. Complete baseline separation was not achieved for all components under the finally selected operating conditions as a balance was sought between optimum separation *versus* GC analysis runtime.

Marginal peak tailing effects were found to be a function of the multiple connections inherent in the chromatographic system design. These could be reduced by looping 1 m from the front end of the column up the heated transfer line jacket and connecting it directly to the cold trap exit, so removing the deactivated transfer line completely[23]. Cryofocussing was found to result in enhanced sensitivity and improved resolution of all components[24]. Overall system stability was found to be nearly constant. Retention data values for 26 key components typical of those found in petroleum-related "process" activities are presented in Table I. Relative response factor constancy *versus* concentration was observed for all components over a six month time period for calibration components of similar polarity[25].

At temperatures lower than −35°C, all components with boiling points between methane and *cis*-butene-2 exhibited excessive band spreading and comparitively small relative peak areas. This was attributed to condensation effects on the column and breakdown in the internal flow dynamics and therefore separating characteristics of

TABLE I

RETENTION TIME DATA FOR 26 COMPONENTS SELECTED AS KEY REPRESENTATIVE MATERIALS FOUND IN TYPICAL PETROLEUM RELATED SAMPLES

Standard deviation data based on 10 runs.

Peak No. (Fig. 1)	*Component*	*Retention time (min) ± S.D.*	*Peak No. (Fig. 1)*	*Component*	*Retention time (min) ± S.D.*
1	Methane	1.72 ± 0.02	14	*n*-Hexane	17.24 ± 0.02
2	Ethylene	1.93 ± 0.01	15	Benzene	18.17 ± 0.03
3	Ethane	2.16 ± 0.02	16	*n*-Heptane	18.86 ± 0.02
4	Propylene	3.30 ± 0.02	17	Toluene	19.75 ± 0.03
5	Propane	3.51 ± 0.02	18	*n*-Octane	20.39 ± 0.02
6	Isobutane	4.86 ± 0.03	19	Ethylbenzene	21.29 ± 0.04
7	Isobutylene	7.82 ± 0.02	20	*m*-Xylene	21.38 ± 0.03
8	*n*-Butene	7.93 ± 0.02	21	*o*-Xylene	21.81 ± 0.02
9	1,3-Butadiene	8.46 ± 0.03	22	Isopropylbenzene	22.32 ± 0.04
10	*n*-Butane	8.98 ± 0.02	23	*n*-Propylbenzene	22.74 ± 0.02
11	*trans*-Butene-2	10.36 ± 0.02	24	1,3,5-Trimethylbenzene	23.01 ± 0.02
12	*cis*-Butene-2	11.89 ± 0.02	25	1,2,4-Trimethylbenzene	23.47 ± 0.03
13	*n*-Pentane	15.16 ± 0.03	26	1,2,3-Trimethylbenzene	23.91 ± 0.03

the column at −40°C. SGE do not, however, state a minimum operating temperature for the BP-1 column.

Utilising the finally selected GC conditions it was also possible to achieve complete separation of homologous C_5, C_6 and C_7 branched isomers spiked into the basic calibration mixture within the 25-min analysis time. It was also possible to run the column up to 300°C to separate *n*-alkanes up to C_{14}. Separation of homologous alkenes (olefins) is also feasible by reducing ramp rate 2 to 5°C per min.

Perkin-Elmer claim the ATD-50 can process samples whose boiling points range from −90°C to +300°C (ref. 22), the extremely narrow concentrated band of sample eluting from the cold trap exit port being wholly compatible with most types of GC analysis. With the exception of methane (boiling point −180°C), the ATD-50 was found to be at least capable of coping with samples whose boiling points are as low as −110°C (*i.e.* ethylene, −109.3°C).

This method is now used routinely in the laboratory and has proved exceptionally reliable, having been used to analyse over 200 liquefied petroleum gas samples either as adsorbent trapped airborne vapours or as liquid "process" samples.

CONCLUSION

The comparitively high analytical system efficiency achieved by combining a thermal desorption system, cryogenic methods and high-resolution capillary GC has much to commend to the petroleum environmental chemist. The simultaneous analysis of complex mixtures containing materials ranging from ethylene to substituted benzenes pose complex analytical challenges. Although the laboratory already equipped with an automated thermal desorber should have little difficulty in adopting this system, the method is easily transposable to an ordinary gas chromatograph with

cryogenic facilities at minimum cost. In effect, the method offers (1) a simple one-step technique, (2) significant analytical flexibility, (3) excellent relative retention time reproducibility and (4) quick turnaround on analysis time.

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