MULTIELEMENT TRUE BOILING POINT GAS CHROMATOGRAPH FOR MONITORING OIL POLLUTION

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ABSTRACT

A true boiling point gas liquid chromatograph (GLC) has been designed to measure simply and conveniently GLC data for all types of petroleum streams, including crude oils and residual fuels which contain considerable portions of high-boiling materials. The instrument generates simultaneous carbon and sulfur boiling point profiles up to 538°C (C_{42}). A quantitative measure of the nonvolatile organic portion of the sample is achieved by backflushing and combusting the material remaining in the inlet. Thus, identification of oil pollution samples is facilitated by obtaining data on the carbon and sulfur distribution and the amount of residue in a single, rapid analysis. Under certain circumstances, the total recovery capability also permits the extent of weathering of oil pollution samples to be determined directly from the chromatographic results.

INTRODUCTION

A key ingredient in any scheme for preventing and controlling oil pollution is a reliable means for monitoring and identifying the pollutant and its source. Many techniques have been proposed including adsorption chromatography, molecular emission and absorption spectrometry, atomic absorption spectrometry, gas chromatography, mass spectrometry, metals analysis, and carbon and sulfur isotope ratios [1,2]. These techniques range from those which can be carried out in most laboratories, such as gas chromatography, infrared, and fluorescence spectroscopy, to those which require complicated equipment and sophisticated techniques not generally available. Since it would be highly desirable to have a technique which was generally available and readily installed in a variety of locations, including mobile laboratories, gas chromatography has become increasingly attractive [3,4]. However, the usual gas chromatograph provides only a carbon boiling point profile of the more volatile components. This information is not usually sufficient for complete identification of an oil pollutant. Recently, the power of the gas chromatographic technique has been considerably enhanced by incorporating another detector capable of measuring a sulfur boiling point profile [5,6,7]. The combined carbon and sulfur profiles are quite effective for use in matching unknowns with suspected pollution sources. The sulfur profile has the additional feature of being less susceptible to weathering [1].

Since simultaneous carbon and sulfur gas chromatography appears to be one of the best available techniques, it was desirable to develop an instrument embodying as many useful features as possible. Amongst these are the following:

1. capability for measuring as high boiling components as possible
2. direct measurement of the residual organic material without weighing or use of internal standards
3. detector responses independent of compound type
4. simple, rapid, repeatable operation.

Approach

Experience had shown that carbon boiling point profiles to 538°C (C_{42}) and a direct measure of the nonvolatile residue could be obtained with a gas chromatograph [8]. The necessary equipment consisted of a programmed temperature column from which the effluent passed into a furnace containing a tube filled with copper oxide to convert organic components to CO_2 thereby eliminating the need for response factors for the thermal conductivity (TC) detector. The system was arranged so that the column could be backflushed to remove material that had not passed completely through the column, and at the same time, the injection port temperature could be raised while introducing oxygen to oxidize nonvolatile organic residue. Thus, total recovery of the organic material was obtained. If a flame photometric detector (FPD) could be added to such an instrument, the sulfur compounds could be measured simultaneously. However, the tube filled with copper oxide is not compatible with repeatable quantitative sulfur recovery due to both chemical and physical interactions of the sulfur species with the metal tube and copper oxide. Therefore, the copper oxide-filled tube was replaced with an oxygen-charged quartz combustion tube. Sulfur compounds could now be reliably detected with the FPD, but the TC detector was exposed to varying concentrations of oxygen which reduced its response to the CO_2 produced from the combustion of the carbon-containing materials. This problem was circumvented by using a nondispersive infrared (NDIR) detector sensitized for CO_2. The resulting multi-element true boiling point (ME-TBP) gas chromatograph generates in a single analysis simultaneous carbon and sulfur boiling point profiles up to C_{42} and a quantitative measure of the nonvolatile organic portion.

Instrument design

The ME-TBP apparatus is a self-contained unit. All the necessary controls for adjusting the detectors, the program, or the gas flows are readily accessible. Special effort was made to compact the apparatus within practical limits in order to keep electrical and transfer lines as short as possible.

The principal components of the apparatus are the gas chromatograph, the nondispersive infrared detector, the flame photometric detector, the temperature programmer and control circuitry, the chart recorder, and the gas flow controllers. Interconnection of these components is shown in the functional block diagram of figure 1 and the flow diagram of figure 2.

The gas chromatograph. The gas chromatograph (GC) consists of the injection port, column oven (with backflush valve), and the combustion oven. The injection port of the GC is fabricated of Inconel 600 tubing lined with quartz tubing secured with ceramic adhesive. Gas supply enters via a U-shaped tube placed along side the quartz combustion tube. The GC column is located between
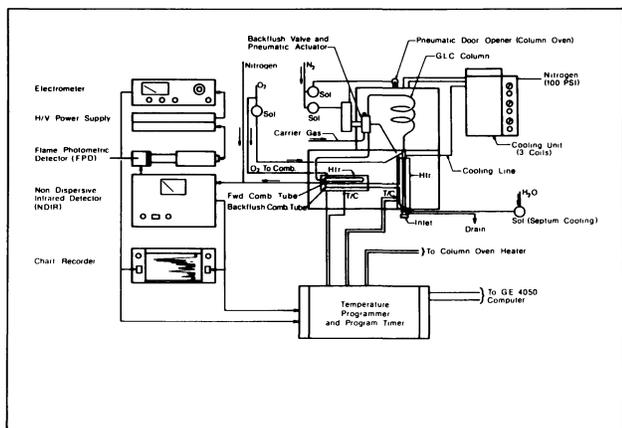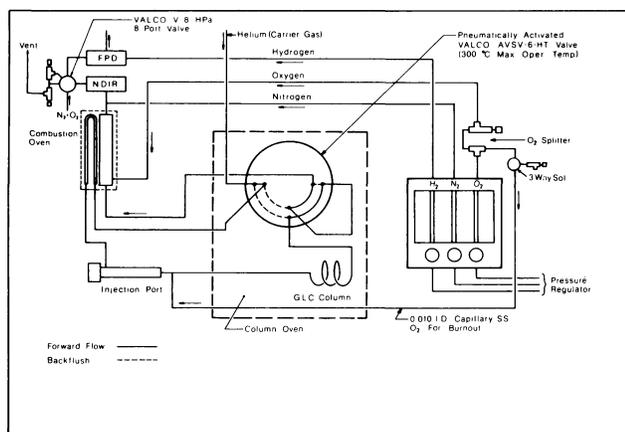
Figure 1. Functional block diagram ME-TBP

Figure 2. Flow diagram ME-TBP

Detectors. The organic materials are converted to CO_2, SO_2, water, etc., in the oxygen-charged combustion tube. The presence of excess oxygen in the effluent places limitations on the type of detectors which can be used. Thermal conductivity detectors, so eminently suited for the copper oxide technique, are not useful due to the presence of oxygen in the effluent which reduces the detector sensitivity to a level where its operation is marginal. Therefore, a Mine Safety Appliances Co. LIRA Model 202 NDIR unit sensitized for CO_2 with a span of 0-1500 ppm was selected. The NDIR will not respond to nitrogen, oxygen, and helium (principal components of the effluent) since they do not adsorb infrared energy. Certain combustion products, e.g., water, do not cause any interference due to their low concentration in the effluent. Additional components in the effluent are such that they adsorb infrared energy in a widely different spectral region than CO_2. The effluent ($\sim$ 100 ml He and 40 ml O_2) is diluted by nitrogen ($\sim$ 150 ml) before entering the NDIR. Nitrogen is added to reduce the residence time and to sharpen peaks in the detector. Teflon tubing is used to connect the combustion tube with the NDIR.

Sulfur in the sample is detected by a Tracor FPD mounted adjacent to the NDIR. The electrometer is a Keithley Model 414S. Gases for the flame are supplied through flow controllers and rotameters calibrated for hydrogen, nitrogen, and oxygen. Nitrogen and oxygen are blended (air is not used) in a ratio to maintain a hydrogen-rich flame which is needed for good sulfur sensitivity.

An effluent splitter was also added between the NDIR and the FPD as shown in figure 2. This was necessitated by the inability of the FPD to handle large sulfur concentrations. As a result, low sulfur samples are run directly without splitting, while high sulfur samples are split 10:1. Since the detector's oxygen supply comes directly from the effluent, additional O_2 and N_2 have to be supplied through a "make-up" line when the splitter is used. This make-up of O_2 and N_2 is taken directly from the pressure regulators ahead of the flow controllers and rotameters of the FPD. The make-up flows need to be preset only once for a fixed split ratio. An 8-port switching valve changes streams and cuts the make-up lines in and out with a single turn.

Temperature programmer and timing circuitry.

The digital linear temperature programmer for the column oven and the two isothermal temperature controllers (injection port and combustion tube) are located on a single chassis. Pulses derived from a high frequency clock via a frequency synthesizer are used to generate the temperature program. Digital counters and comparators are used to program the system for various isothermal functions, e.g., isothermal hold, upper temperature limit, cooling of the column oven at end of run, etc. In addition, the digital temperature programmer can be used for the control of solenoid valves, etc., during a program cycle. Operation of such a temperature programmer is straightforward. Push buttons initiate start, hold, and reset functions. Thumbwheel switches are used to set the temperature programming rate, as well as the initial, isothermal hold, and final temperature settings. They are also used to set time delay for isothermal hold which occurs during programming and to activate backflush and various solenoids.

Data acquisition. Data acquisition is influenced by the fact that both the NDIR and the FPD have nonlinear responses. For the work reported in this paper, the nonlinearized detector signals were displayed on the dual pen recorder, while the same signals were linearized and integrated in a computer.

Data acquisition and interpretation can be handled with present day electronic hardware in a number of ways not requiring an elaborate computer system. Thus, the detector responses can be linearized and considerable deduction made from the chart traces alone. Integration techniques are numerous and well known in GC practice and can be used for rapid quantitative data gathering.

Operation

Typical operating conditions for the ME-TBP are summarized in table 1. A blend of n-alkanes (nC_5 through nC_{50}) is used to calibrate the unit. The standard blend ($\sim$ $2\mu\ell$) is injected at $0°C$ column temperature. Following injection, the column is programmed at

the injection port and the backflush valve. Gas flow through the backflush valve is shown in figure 2. The valve is located in the column oven and is pneumatically operated. To counteract any temperature over-ranging of the GC column during programming, an electro-pneumatic relay is interlocked with the heater to introduce dry-ice cooled nitrogen into the column oven. The rate of cooling is inversely proportional to the voltage applied to the heater element. During backflush, the sample inlet is heated from $325°C$ to $700°C$, and $\sim$ 20% of the oxygen from the combustion tube is diverted to the injection port to ensure complete residue recovery. Oxygen flow is controlled by a solenoid as shown in figure 2. To protect the septum, a single turn of 0.126-inch outside diameter (OD), thin wall stainless steel tubing is welded to the inlet just behind the septum cap. Water circulates through this cooling line when the unit is being backflushed. Water flow is turned on/off by a solenoid. After backflush is completed, the injection port is cooled with a high flow rate of dry-ice cooled nitrogen. Also, the column oven door is pneumatically opened at the end of the program cycle, and a large volume of dry-ice cooled nitrogen is blown into the oven housing to facilitate cooling. Cooling time from $\sim$ $335°C$ to $0°C$ is $\sim$ 6 minutes.

The quartz combustion tube ($\sim$ 15 mm OD X $\sim$ 16 cm) is connected to the six-port valve with Cajon flexible glass to metal tubing. Its temperature is maintained at $\sim$ $900°C$ with a cylindrical heater. Effluent from the GC column enters the oxygen atmosphere in the combustion tube through a 1-mm inside diameter (ID) nozzle. Oxygen is introduced into the combustion tube via a 1 mm ID quartz capillary. The injection port and the combustion oven are mounted in the same enclosure and are separated by insulation. Also, the injection port and combustion tube housing and the column oven are mounted on a common platform forming a single integral part of the ME-TBP.

Table 1. Typical operating conditions

Column	40" x ⅛" O.D.
Packing	6% SP-2100 on Supelcoport 80/100 mesh
Sample Size	1-5 μl
Program Rate	5°C/minute
Initial Temperature	0°C
Final Programmed Temperature	325°C
Backflush Temperature	335°C
Flow Rates	
Helium	75-100 ml/minute
Oxygen to Combustion Tube	30-40 ml/minute
Oxygen to Inlet (Burn Out)	~20% of Comb. Tube O_2
Nitrogen	150 ml/minute
Hydrogen (FPD)	80-100 ml/minute
Unit Temperatures	
Combustion Tube	900°C
Injection Port (Forward Flow)	325°C
Injection Port (Backflush)	700°C

5°C/minute to 325°C and held isothermal until nC_{42} (BP 538°C) elutes. At the apex of the nC_{42} peak, the column is backflushed. Upon backflush, the column temperature and the injection port are inertia programmed to 335°C and 700°C, respectively; also, oxygen is introduced into the injection port to combust all the organic residue. From the resulting chromatogram shown in figure 3 a calibration curve of retention time versus true boiling point is constructed. If the run parameters are held constant, one calibration per week has proven adequate. Boiling points for the organic sulfur compounds are determined based on the calibration curve of the carbon compounds.

The ME-TBP can be utilized for analyzing a variety of samples from light naphthas to full-range crudes, including both liquid and solid materials. Viscous liquids and solids, e.g., pitch, tar, or oil-covered sand, etc., are introduced into the inlet with a sample boat. Since the unit gives total sample recovery, weighing is not necessary. Typical results for two diesel fuels are given in figure 4. Marked differences are apparent in both the carbon and sulfur profiles. Together, the profiles provide definitive fingerprints of each sample. These two diesel fuels were suspected of being the source of an unknown. Comparison of the ME-TBP fingerprint for the unknown with those shown in figure 4 provided strong evidence as to the source. An actual oil spill sample and the suspected crude oil source are shown in figure 5. With due allowance for the effects of weathering, it is clear that the crude oil could be the source of the spill.
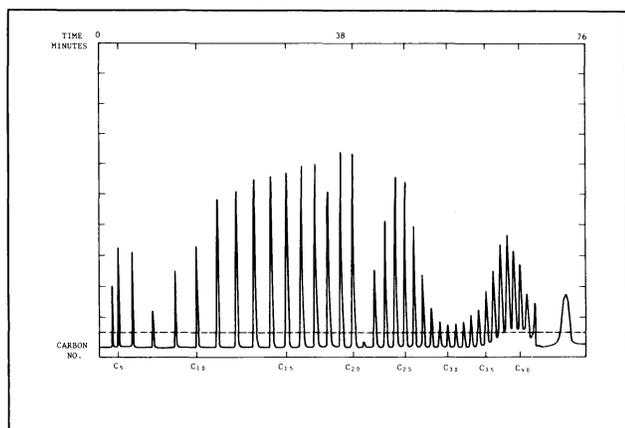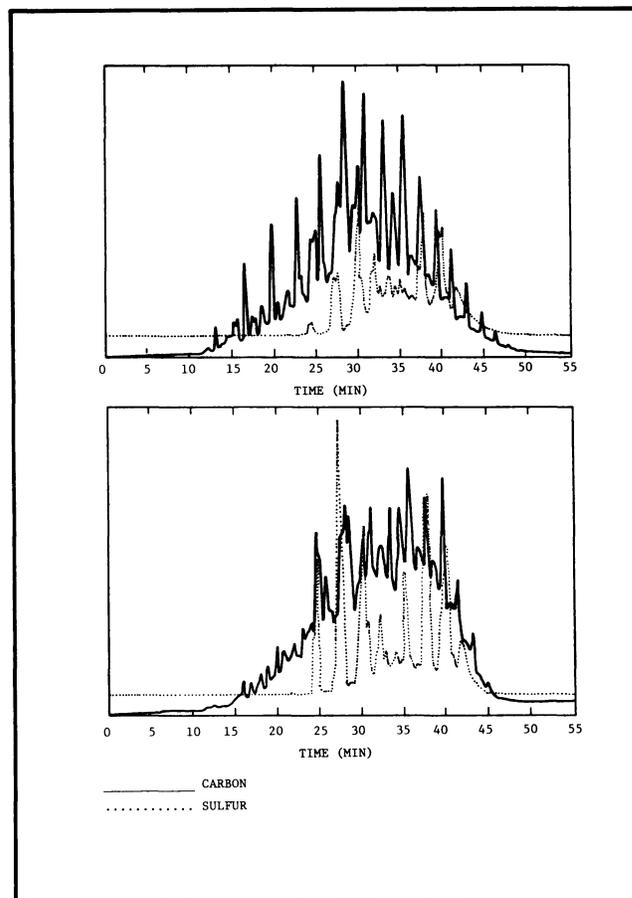

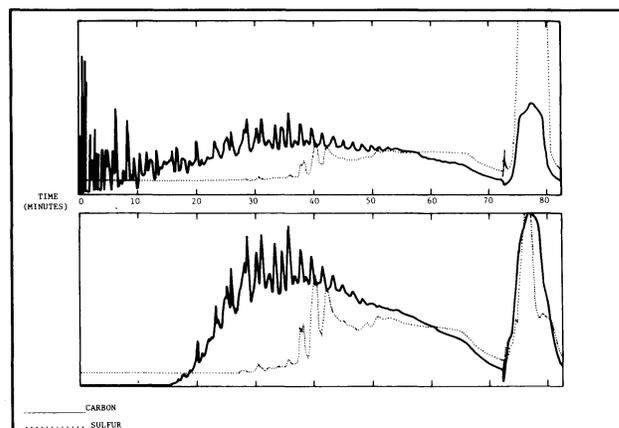Figure 4. Comparison of diesel range material by ME-TBP

Figure 5. ME-TBP chromatogram of weathered oil spill sample (lower trace) and suspected crude oil source (upper trace)

Weathering

Another important aspect of oil pollution monitoring is measurement of the extent of weathering. This can provide valuable information concerning the fate of oil spills or seepage and can provide guidance for cleanup operations. A number of processes are involved in weathering such as evaporation, emulsification, dissolution, auto-oxidation, and biological degradation. In many instances, evaporation will be the major phenomenon occurring. When this is the case, Sivadier and Mikolaj [9] have developed a gas

Figure 3. ME-TBP calibration

chromatographic method for measuring the extent of evaporation. Their results show that the method is an effective and accurate means for obtaining quantitative data. Use of the multielement true boiling point gas chromatograph with total sample recovery greatly simplifies the method. To apply the technique, certain criteria must be met.

1. The pollution source must be identified and a sample available.
2. The pollutant should be from a single source.
3. Evaporation should be the major cause of weathering.

The use of the ME-TBP for identification of the pollution source has already been described in this paper. Qualitative examination of the carbon and sulfur boiling point profiles of the pollutant and source material will generally indicate whether the last two criteria have been met.

The technique for obtaining a quantitative measurement of weathering is based on a comparison of the observed percent of nonweathered carbonaceous residue in the gas chromatograms of the source material and the weathered pollutant. Since response factors for different compound types are not required and since all the carbonaceous material is recovered, one can write two equations:

$$M_v^o + M_r^o = 100, \tag{1}$$

$$M_v + M_r = 100. \tag{2}$$

where M_v^o and M_r^o are the weight percent volatiles and residue, respectively, in the pollution source and, similarly, M_v and M_r are the corresponding weight percents for the weathered pollutant. The boiling point delineating between volatiles and residue must be the same for both materials and is selected on the basis of observation so that volatiles and residue in both samples are reasonably large percentages and such that there has been no loss of volatiles from M_r. When this latter condition is met, then M_r and M_r^o have the same composition and one can apply a scale factor (M_r^o/M_r) to the weathered sample so that the two samples can be directly compared. Multiplying (2) by this factor one obtains

$$M_v\left(\frac{M_r^o}{M_r}\right) + M_r^o = 100\left(\frac{M_r^o}{M_r}\right) \tag{3}$$

Now that the samples can be compared, the loss can be expressed as the difference between the volatiles portions of each sample:

$$\% \text{ Loss} = M_v^o - M_v\left(\frac{M_r^o}{M_r}\right). \tag{4}$$

Substituting equations (1) and (3) in (4)

$$\% \text{ Loss} = 100\left(1 - \frac{M_r^o}{M_r}\right). \tag{5}$$

Thus, the percent loss can be calculated directly from the results of two chromatographic analyses.

To check the validity of this technique, two full-range crudes were each subjected to precision distillation on a 30-plate 1" Oldershaw column to remove known amounts of overhead material (volatiles). Three different overhead cuts were taken and the residues after each cut were analyzed by the ME-TBP unit, as was the original crude. The measured and calculated results for each cut are summarized in table 2. As indicated in the discussion of this technique, the selection of boiling point between volatiles and residue should be high enough so that there has been no loss of volatiles from the residue. There is considerable evidence that evaporative weathering occurs mostly below 600°F [5,6,9]. Therefore, this is usually a suitable boiling point to select for the residue.

Table 2. Determination of simulated weathering with the ME-T|

Crude	Distillation		ME-TBP Calculated % Overhead	
	Cut Temp (°F)	% Overhead	600+ Residue	1000+ Residue
East Texas Sweet	300	15	18	-
	518	39	41	40
	600	50	-	49
West Texas Sour	292	22	22	-
	518	43	46	45
	600	51	-	49

Since the ME-TBP is backflushed at 1,000°F, this is another convenient point to take for the residue. If either the residue or volatile percentages become too small, the accuracy of the method decreases. Thus, for the low % overhead (lightly weathered) samples, the 1000+ residue was not considered. For the high % overhead (heavily weathered) samples, the 600+ residue was not used. When comparing a weathered pollution sample with the source material, it is usually apparent where to select the delineation between volatiles and residue. Comparison of the calculated and observed results in tabel 2 indicates good agreement.

CONCLUSION

A multielement true boiling point gas chromatograph has been developed which generates simultaneous carbon and sulfur boiling point profiles up to C_{42} and also directly determines the residue. The instrument has to be proved effective in fingerprinting petroleum streams and identifying sources of oil pollution. In certain instances, it can also provide a quantitative measure of weathering.

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