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Note

Direct determination of corrosion inhibitor in aviation fuel by a column-switching technique using gel-permeation chromatography

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Hitec E580 is added to aviation fuel as an antiwear agent and corrosion inhibitor. The normal concentration range is 10–20 ppm and the level may be determined by measuring the concentration of the major active ingredient, namely dimer acid (technical-grade dilinoleic acid).

The method of Hillman *et al.*[1] involves multiple extractions of the dimer acid from a large volume of fuel and measurement is achieved by gel-permeation chromatography (GPC) with refractive index detection. A modified version of this method has been used to determine the concentration of a range of similar corrosion inhibitors in jet fuel and to examine the depletion of the active ingredient on contact with sea water and metal surfaces[2,3]. A method using reversed-phase ion-exclusion chromatography with UV detection has also been described[4].

Hillman *et al.*'s method[1] cannot be applied to the small amounts of fuel, 10 ml or less, which may be all that is available as part of an accident investigation. Also, the manual extraction steps are time-consuming and cannot be readily automated. This paper describes an improved method of measuring Hitec E580 in aviation fuel which overcomes these problems. The method uses an on-line precolumn, containing a polar packing, to extract the dimer acid from the fuel. Operation of a switching valve allows the precolumn to be flushed with tetrahydrofuran (THF), thus transferring the dimer acid to a GPC column. Refractive index detection is used. The two methods give results which are in acceptable agreement.

EXPERIMENTAL

Apparatus

The apparatus consisted of two Waters 510 reciprocating pumps, one directly connected to a Waters automated switching valve and the other connected to the valve via a Rheodyne 7120 sample injector fitted with a 2-ml loop. The switching valve was fitted with a Waters Guard-Pak precolumn module containing a cyano insert. Separations were carried out on a 50-Å and a 100-Å PL-Gel column (250 mm × 4.6

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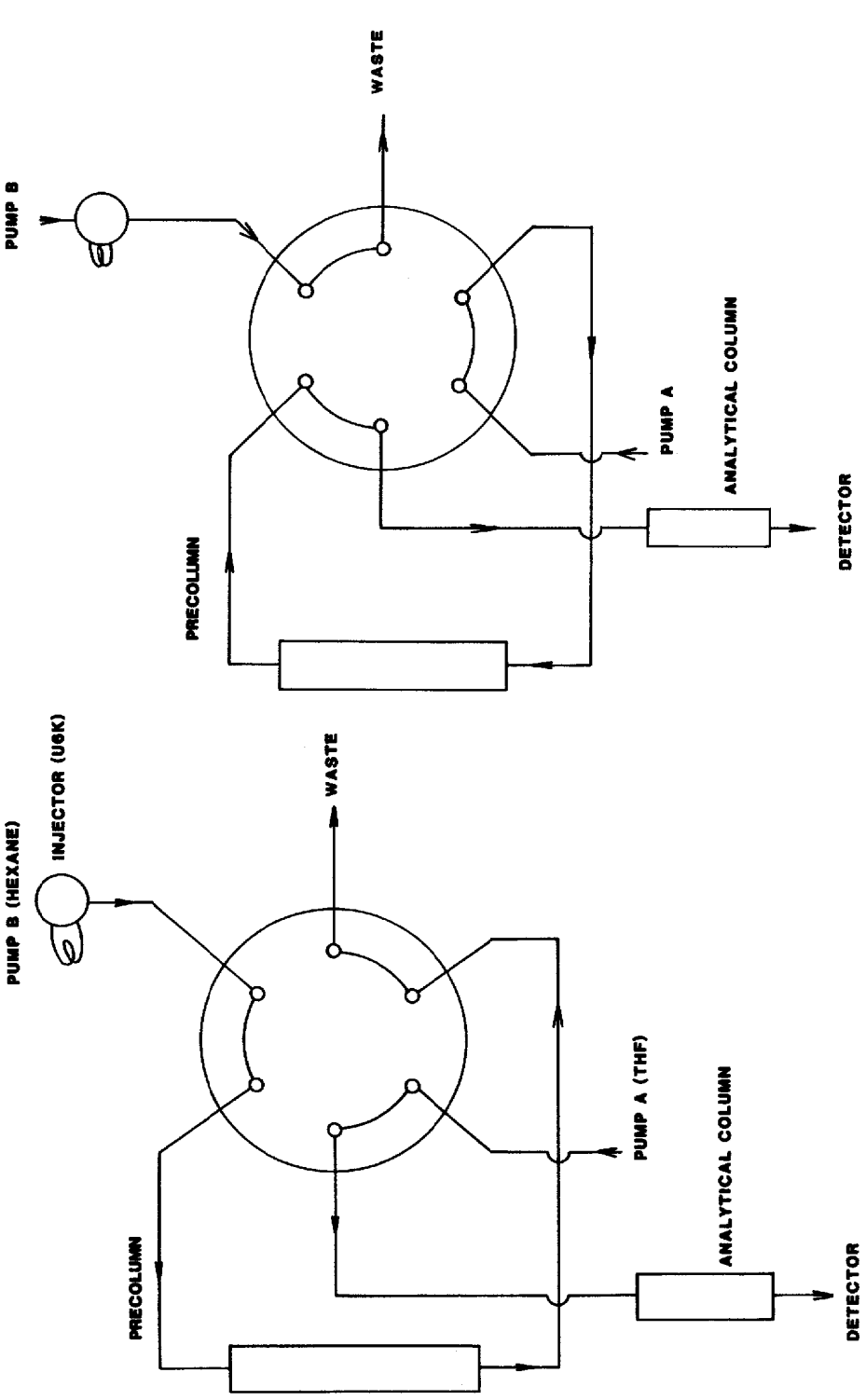

Fig. 1. (A) Rheodyne valve in configuration 1 (load precolumn). (B) Rheodyne valve in configuration 2 (flush precolumn).

mm I.D.), containing 5-μm packing, connected in series. The detector was a Waters 410 differential refractometer. System control and data collection were achieved with a Waters 840 data station (see Fig. 1A and B). Unstabilised THF and hexane, both HPLC grade, were obtained from Rathburn (Walkerburn, U.K.).

Procedure

The first stage in the analysis was a combined preconcentration/sample clean-up step; this was required due to the low level of additive present in a large excess of potentially interfering compounds. It was achieved by injecting 2 ml of fuel onto an in-line precolumn containing a disposable cartridge filled with a polar bonded phase packing. The dimer acid was retained on the precolumn and the remainder of the fuel was removed by pumping hexane through the cartridge.

The precolumn module was connected across an automatic switching valve which, when operated, changed the solvent flowing through the cartridge from hexane to THF. This flushed the dimer acid onto the analytical columns and then into the refractive index detector. A sample chromatogram is shown in Fig. 2. The peak eluting just before the main dimer acid peak is believed to be due to trimer acid. The sum of the peak areas was used for quantitation.

Standards were prepared by dilution of a stock solution of Hitec E580 dissolved in an additive-free reference fuel.

RESULTS AND DISCUSSION

The refractive index detector was shown to have a linear response over the required concentration range (Fig. 3). The correlation coefficient was 0.9994.

In order to evaluate the method a number of aviation turbine fuel (AVTUR) samples were analysed. The level of Hitec E580 in these samples has also been determined by the standard extraction method[1]. The results obtained from the two procedures are shown in Table I.

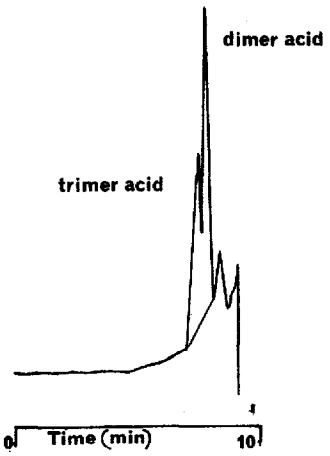

Fig. 2. Chromatogram of Hitec E580 (20 ppm).

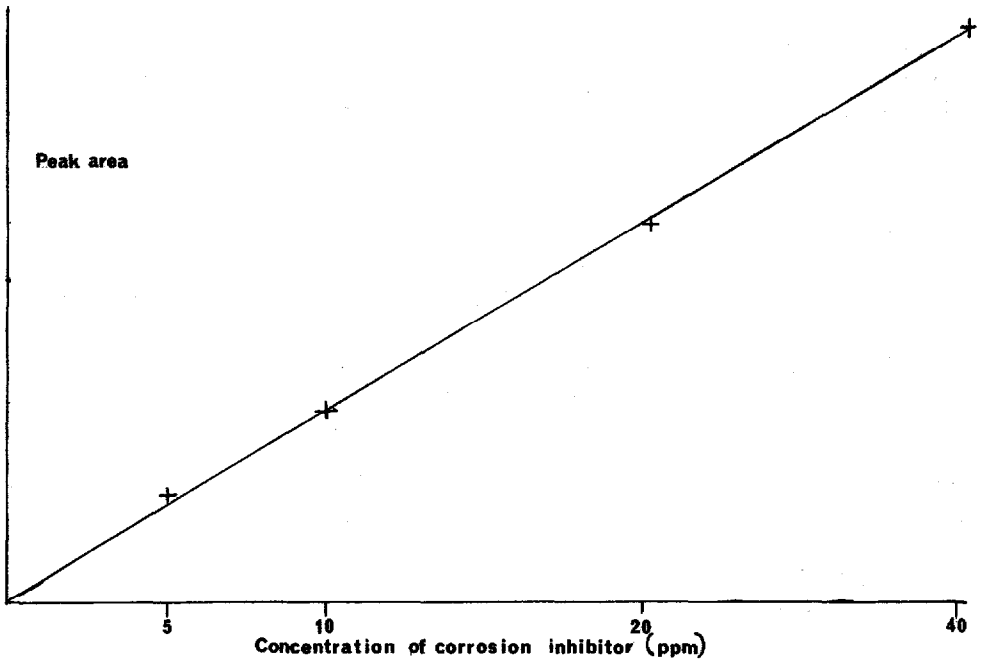

Fig. 3. Calibration curve for determination of Hitec E580 in aviation fuel.

The mean relative standard deviation for the proposed method is 4.1%, which is close to the value of 4.4% reported for the method of Hillman *et al.*[1]. The levels of Hitec E580 found by the two methods are in acceptable agreement.

Sample 5 was markedly different from the other samples in having a deep yellow colour due to ageing. It could not be analysed by the column-switching method due to the presence of a large interfering peak. Old samples can also sometimes cause problems with the extraction method, since the dimer acid peak is only apparent as a shoulder on the side of a large peak arising from co-extracted material.

Both methods were also used to determine the levels of Hitec E580 in AVCAT, the high-flash-point fuel used on ship-based aircraft. Table II shows the results obtained, which are again seen to be in acceptable agreement.

TABLE I

DETERMINATION OF HITEC E580 IN AVTUR SAMPLES

Sample No.	*Concentration of Hitec E580 (ppm)*			
	Extraction method	*Column-switching method*	*Mean*	*Relative standard deviation (%)*
1	11	11.0, 11.5, 11.0, 10.4, 11.0	11.0	3.6
2	12	12.0, 12.5, 12.5	12.3	2.3
3	9	11.0, 10.5, 10.4	10.6	3.0
4	10	11.0, 12.5, 11.0	11.5	7.5
5	11	Interference found	—	—

TABLE II

DETERMINATION OF HITEC E580 IN AVCAT SAMPLES

Sample No.	*Concentration of Hitec E580 (ppm)*		
	Column-switching method	*Mean*	*Extraction method*
1	25, 24	24.5	20
2	39, 40	39.5	40
3	17, 17	17.0	14
4	15, 15	15.0	15
5	15, 14	14.5	14
6	6, 6	6.0	8
7	6, 6	6.0	5

CONCLUSIONS

A method has been developed for the quantitative determination of dimer acid, and hence Hitec E580, in aviation fuel. The accuracy and precision are close to that of the standard extraction method, and it has the following advantages.

(i) Only 2 ml of fuel are required, compared to 800 ml in the extraction method. This makes the new method suitable for use with the limited amounts of fuel which may be available in an accident investigation.

(ii) The elimination of the manual extraction steps means that the new method is faster and more convenient to operate.

(iii) The method can be fully automated.

The equipment used in this investigation included a detector with a very high signal-to-noise ratio. The estimated limit of detection was 1 ppm Hitec E580 (which corresponds to a dimer acid concentration of around 0.4 ppm). If a less sensitive detector is used then a larger sample volume is required, in order to maintain the same limit of detection. The upper limit of sample volume is provided by the breakthrough volume of the precolumn insert.

Several other commercially available corrosion inhibitors/lubricity additives are based on dimer acid, and the column-switching method is expected to be suitable for their determination. However, one additive is known to contain other dibasic acids in addition to dimer acid, and the method has not been extended to the examination of this type of sample.

ACKNOWLEDGEMENTS

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