Thomas A. Kubic,[1] *M.S., J.D. and Francis X. Sheehan*,[2] *B.S.*

Individualization of Automobile Engine Oils II. Application of Variable Separation Synchronous Excitation Fluorescence to the Analysis of Used Automobile Engine Oils

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ABSTRACT: Forty-five used automobile engine oils were analyzed with conventional fluorescence techniques as well as synchronous excitation and variable separation synchronous excitation fluorometry. Only two samples were considered to be indistinguishable in this group of samples. The high sensitivity, nondestructiveness, and rapidity of these procedures, coupled with their high discriminating power, make fluorometry a method that can be recommended in forensic oil individualization.

KEYWORDS: criminalistics, petroleum products, luminescence

Kubic et al demonstrated the value of fluorometry for the forensic science examination of auto engine oils [*1*]. They were able to establish the high discriminating power of luminescence techniques used to individualize new (unused) automobile engine oils. These lubricants are composed principally of aliphatic and aromatic hydrocarbons with various additives to improve lubricating qualities and increase stability.

Used automobile engine oils contain fluorescent polynuclear hydrocarbons produced by combustion and pyrolysis in addition to the components normally found in the unused oils. Begeman and Colucci [*2*] have found that more than 5% of the radioactive benzo[*a*] pyrene-8-9-^{14}C that was added to the gasoline of an automobile accumulated in the crankcase oil along with other Carbon-14 compounds. It is reasonable to conclude that a great variety of compounds found in gasoline would accumulate similarly in the engine oil reservoir. This has been confirmed by Lloyd [*3*, pp. 235-253] who has separted approximately 50 polynuclear hydrocarbons from used automobile engine oils and found them to be fluorescent. An exhaustive study of the hydrocarbons present in unused petroleum products has been published by Rossini [*4*].

Other workers have found that polynuclear hydrocarbon exhaust emissions may be dependent on engine mileage [*5*], engine type [*6*], and the presence of various gasoline additives [*7*]. Although these experiments were concerned with exhaust emissions, it seems reasonable to assume, in the light of Begeman and Collucci's findings, that these factors also affect the

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[1]Detective criminalist, Scientific Investigation Bureau, Nassau County Police Department, Mineola, NY.
[2]Graduate student, John Jay College of Criminal Justice, New York, NY.

accumulation of polynulcear hydrocarbons in used crankcase oil. Lloyd [*3*, pp. 235-253] suggests that operating temperatures and the concomitant degree of oxidation of the oils further add to the total quantity and proportions of these hydrocarbons. Since degradation and oxidation products are variably dependent on the combination of conditions to which a particular engine has been subjected, individualization of the crankcase oil should be possible and fluorometry seems to be a logical approach.

Experimental Procedure

The instrument employed in these studies was a Farrand Mark I spectrofluorometer. Its characteristics as well as the operational parameters used in this study are essentially identical with those described by Kubic et al [*1*].

The automobile engine oil samples were collected from the dipsticks of 45 vehicles assembled in a public parking lot in Nassau County, Long Island, NY during the summer of 1979. No attempt was made to include or exclude any particular oil brand or type, nor any particular engine type or size. The use period of the oil either in mileage or time was likewise not considered.

The samples were stored in glass test tubes sealed with corks, after collection. For analysis, the oil was diluted to approximately 100 ppm (w/w) with cyclohexane (Mallinckrodt spectroquality) and stored in glass test tubes with aluminum-lined screw caps. The solvent as supplied was found to be satisfactory without further purification.

The samples were first examined by conventional fixed excitation wavelength fluorometry at exciting wavelengths of 254 and 290 nm. Synchronous excitation fluorometry, the method pioneered by Lloyd [*3*, pp. 83-96], was then used with a wavelength λ separation of 23 nm ($\Delta\lambda = 23$ nm). Finally each oil was examined by variable separation synchronous excitation fluorometry (VSSE) [*1*] technique with angles and initial $\Delta\lambda$ as follows: 50.2°/20 nm, 56.3°/30 nm, and 59.0°/30 nm. Those samples that were not individualized at this point were analyzed by the VSSE technique employing 67.4° scan with initial $\Delta\lambda$ of 40 nm.

Results and Discussion

To determine the discriminating power of each individual fluorometric technique as well as that for the total method, which is a combination of all the individual techniques, the following coding scheme was devised.

As each fluorometric technique was used, those samples that were similar by that technique were grouped together and assigned an identification code letter. For example, after all the samples were analyzed by fixed excitation at 254-nm emission fluorometry they were divided into eight groups and coded A through H. This letter designation appears as the extreme left letter under "Group" on Table 1. After the second analysis a fixed excitation at 290 nm was completed the samples were similarly divided into four groups and coded A through D. This code letter appears as the second letter left to right under "Group" in Table 1. These code letters when they appear in different columns (left to right) are independent identifiers and therefore two samples coded AB and BA would be distinguishable. After multiple techniques were used those samples that possessed identical letter coding, considering both letter and column position were considered indistinguishable while any difference in the total code indicated that the sample could be differentiated. For example, after five techniques were used two groups might be coded AAAAB and AAAAC thus indicating that the samples or groups were indistinguishable by the first four techniques but were differentiated by the last method. Over 400 individual spectra were determined and spectra were considered "similar" if: (1) all peaks occured within 5 nm of each other and (2) relative intensities when compared to the largest peak were within 10%.

Table 1 displays the coded data obtained from the first six fluorometric techniques

Table 1—Combination of 254 nm, 290 nm, synchronous, and VSSE[a] subgroups.

Group[b]	No. Oils in Group	Group	No. Oils in Group
AAADBD	1	BBCAAA	1
AAADDD	1	BBCBAA	1
AAAFBD	2	CAACBE	1
AAAFED	1	CAAFBE	1
AAAFEE	1	CAFCBE	1
AAAHBE	1	CAFFEE	1
AAEHBD	1	CEAGEE	1
AAFFEE	1	DADEEE	1
AAFHED	1	EAAGED	1
AAFJEE	3	EAAGEE	1
ACFHED	3	FAADDB	1
ACFHEE	4	FAAFDC	1
ACFJEE	2	FAAFDD	1
ACGHED	3	FAAFED	1
ACGHEE	1	FABFDD	1
ACGHEE	1	GAAFCE	1
ADFHEE	1	HAFHED	1

[a]50.2°, 56.3°, and 59.0° angles considered.

[b]The first letter indicates the 254-nm subgroup, the second letter indicates the 290-nm subgroup, the third letter indicates the synchronous excitation subgroup, the fourth letter indicates the 50.2° VSSE subgroup, the fifth letter indicates the 56.3° VSSE subgroup, and the sixth letter indicates 59.0° VSSE subgroup.

wherein the 45 samples were subdivided into 34 groups with the greatest number of samples in any group totaling four. As previously noted those groups, 6 of 34, that encompassed more than 1 sample were further analyzed by VSEE employing 67.4° scan with initial $\Delta\lambda$ of 40 nm. Each of these groups was successfully subdivided resulting in individualization of all but two samples from group ACGHED which were indistinguishable. This final subdivision is represented in Fig. 1. All analyses were performed at room temperature without the aid of cyrogenic apparatus that would aid in spectral resolution and therefore may aid in discrimination. Lloyd [*8*] has suggested that deoxygenation of the sample also improves spectral resolution.

Representative spectra obtained employing synchronous excitation and VSSE at 50.2° are presented in Figs. 2 and 3 and 4 and 5, respectively.

Summary

Conventional, synchronous, and VSSE fluorometric techniques have been shown to be powerful methods for the forensic science analysis of automobile engine lubricants. Variable separation synchronous excitation, although the more powerful technique, is not meant to replace conventional or synchronous methods which should be employed first as screening methods.

Likewise, fluorescence methods should not be considered an exclusive tool for the analysis of multicomponent lubricants. However, when used in conjunction with chromatographic methods, infrared spectroscopy and elemental analysis, fluorometry is a uniquely powerful, rapid, simple, and inexpensive analytical technique.

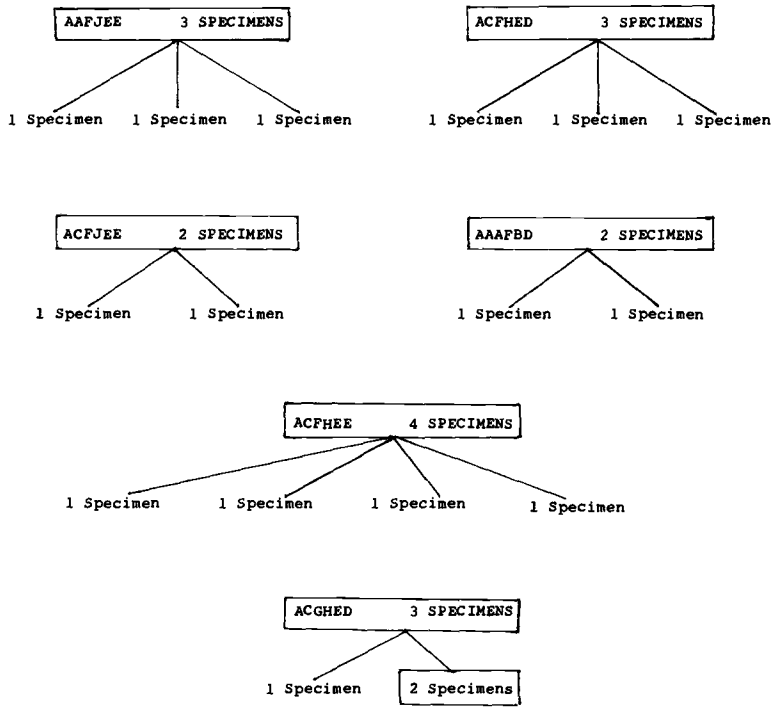

FIG. 1—*Representation of final subdivision of used oil samples by VSSE 67.4°. Two samples remain indistinguishable. Letter code indentifies an oil group and the number gives the number of specimens in that group.*

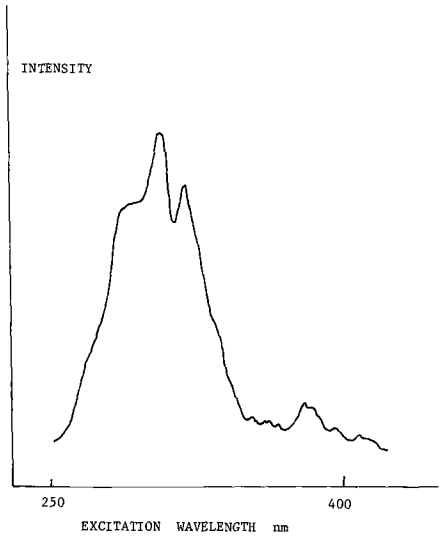

FIG. 2—*Oil Sample 2, synchronous excitation ($\Delta\lambda$ = 23 nm), Group F.*

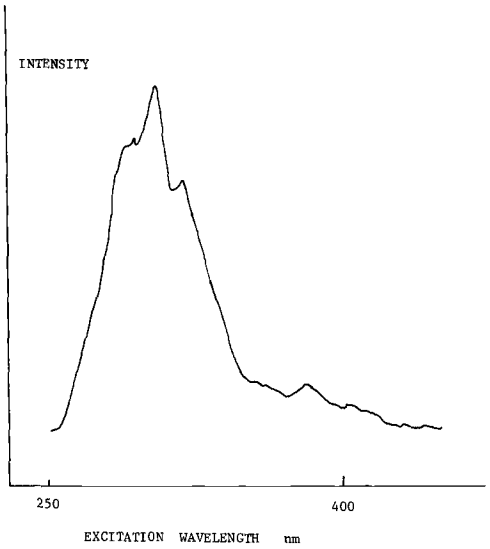

FIG. 3—*Oil Sample 12, synchronous excitation ($\Delta\lambda$ = 23 nm) Group A.*

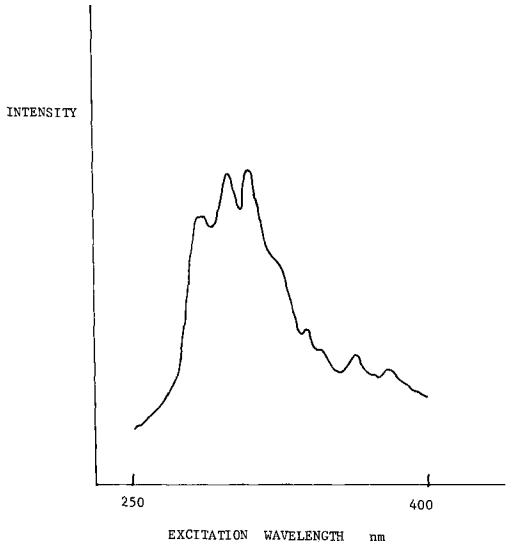

FIG. 4—*Oil Sample 22, 50.2° VSSE, Group H.*

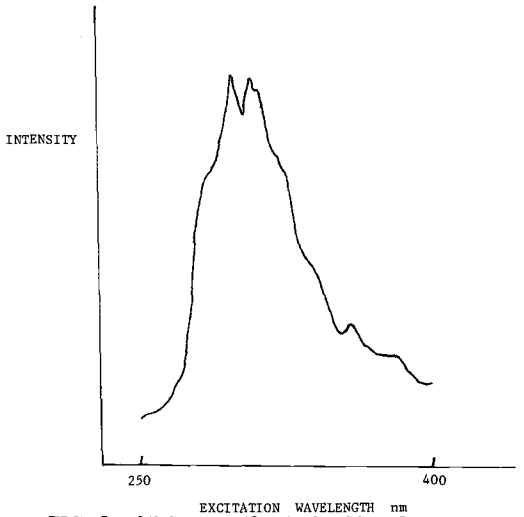

FIG. 5—*Oil Sample 48, 50.2° VSSE, Group I.*

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Address requests for reprints or additional information to
Thomas A. Kubic
Detective Criminalist
Nassau County Police
Scientific Investigation Bureau
1490 Franklin Ave.
Mineola, NY 11501