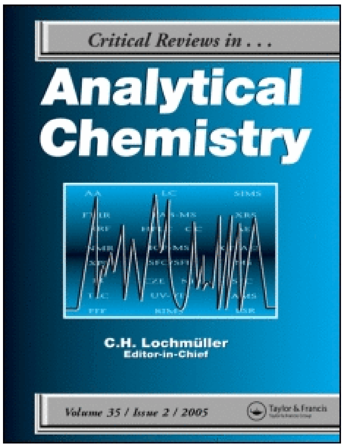

Critical Reviews in Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713400837

The Shopl'skil Effect as an Analytical Tool

Clausius G. de Lima; E. L. Wehry

To cite this Article de Lima, Clausius G. and Wehry, E. L.(1986) 'The Shopl'skil Effect as an Analytical Tool', Critical Reviews in Analytical Chemistry, 16: 3, 177 — 221

To link to this Article: DOI: 10.1080/10408348608542787

URL: http://dx.doi.org/10.1080/10408348608542787

THE SHPOL'SKII EFFECT AS AN ANALYTICAL TOOL

Author: Clausius G. de Lima
Department of Chemistry
University of Brasilia
Brasilia, D.F., Brazil

Referee: E. L. Wehry
Department of Chemistry
University of Tennessee
Knoxville, Tennessee

I. INTRODUCTION

A. Historical Background

A few days after the 60th birthday of the Soviet physicist Prof. Eduard Vladimirovich Shpol'skii, the journal *Doklady Akademic Nauk SSSR* (Proceedings of the U.S.S.R. Academy of Sciences)* received a paper from him together with A. A. Il'ina and L. A. Klimova entitled "Fluorescence Spectrum of Coronene in Frozen Solutions" where it was described that after the authors had examined the fluorescence spectrum of coronene, dissolved in paraffin oil, benzene, and other organic solvents and frozen at liquid air temperature, "an astonishing change in spectrum was observed when n-hexane and n-heptane were used . . . instead of a small number of bands . . . there are a large number of narrow lines which by their width are similar to lines of atomic spectra in gases."[1]

With this and a series of subsequent papers, Shpol'skii and co-workers were opening a new field where the electronic spectra (both absorption and emission) of a large number of polycyclic compounds (when dissolved in certain nonpolar solvents and frozen at low temperature) are characterized by a very narrow spectrum or, as it was called later, a "quasi-linear" spectrum.

According to information published in Soviet scientific journals,[2,3] Shpol'skii's scientific work started in 1911 at the Physics Laboratory of Shanyavskii Moscow City University under the supervision of Prof. Peter P. Lazarev, having as his colleague Sergei Ivanovich Vavilov, who later became known as the founder of the Soviet school of luminescence.[4] At that time, in his twenties, he worked with the chemical effects of X-rays. After World War I — in which he participated as a radiologist — he went back to work with Vavilov and other important physicists at the Institute of Physics and Biophysics of the National Committee on Public Health (which was organized by Lazarev). In the 1930s he started to work at the V. I. Lenin Moscow State Pedagogical Institute where he organized the Optical Laboratory and where he later became Head of the Theoretical Physics Department, until his death at the age of 83 on August 21, 1975.[3]

Besides the discovery — as a result of a careful study related to the luminescence behavior of polycyclic aromatic hydrocarbons (PAH) in low temperature frozen solutions — and further investigation and application of the phenomenon of quasi-linear luminescence and absorption spectra, Shpol'skii worked in photochemistry and in the application of spectroscopy to biophysical and biochemical problems. He also devoted his life first as a co-editor (with Lazarev as Editor) and later as Editor-in-Chief of the

---

* The Physical section is published in English by the American Institute of Physics as Soviet Physics — *Doklady.*

journal *Uspekhi Fizicheskikh Nauk* (Advances in Physical Sciences) and of the Soviet abstract journal *Referatyvnyi Zhurnal Fizika*, and published the book *Atomnaya Fizika* (Atomic Physics) which soon became a very successful textbook.[2,3] The 5th edition was translated into the English language in 1969[5] and was critically reviewed and recommended by Hindmarsh in the appropriate section of the journal *Nature (London)*.[6]

Undoubtedly, of all of Shpol'skii's scientific findings, the Shpol'skii effect (as it was soon called) was a major breakthrough for which he was awarded the S. I. Vavilov Gold Medal from the U.S.S.R. Academy of Sciences in 1962,[2,3] and it opened up a new field of investigation in the area of molecular spectroscopy. Together with Raman and infrared spectroscopy it has helped us to understand the relationship between spectra and structure of several organic molecules. In the area of analytical chemistry, the effect provides a technique which seems to be a powerful tool, principally in the trace detection and determination of PAHs and correlated compounds. The importance of such detection and determination in samples of diverse origin is due to the recognized carcinogenic action of several of these compounds.

B. Fundamental Aspects

As is well known, the use of low temperature in molecular spectroscopy normally improves the resolution, although in glassy matrix the bandwidths are usually in the range of 100 to 400 cm^{-1}. This band character of the emission from glassy matrices has been recognized as being caused by the disordered structure of the glasses; the configuration of the solvent molecules around the solute molecules is, as a result, different, and consequently innumerable different sites or possible configurations of the solvent molecules are created. This leads to a considerable widening of the band. On the contrary, the solvents proposed by Shpol'skii[7-10] are *n*-paraffins, which crystallize very easily during the freezing process, are nonpolar, with a very weak reactivity and in consequence, a small interaction is expected between the usual type of compound (a PAH) and these solvents. The crystalline structure of the *n*-paraffin matrix and the existence of a family of such compounds allow the possibility of an "embedment" of the solute molecules (analyte molecules) in a manner which results in the emission of quasi-lines. The best resolution is usually obtained with one or sometimes four members of the *n*-paraffin family.[11] In such conditions the bandwidths are usually in the 1- to 10-cm^{-1} range. Although there are no general rules for the selection of the best quasilinear solvents, with the polyacenes a similarity between the dimensions of the long axis of these compounds and of the *n*-paraffins results in the best resolution.[7,9,10] For several compounds, however, this rule is not obeyed and other hypotheses have been proposed.[9,10,12-16] As a result of a careful study with coronene, benzo[ghi]perylene, and perylene in *n*-paraffin matrices (at 77, 20, and 4 K, respectively) Pfister[12,13] concluded that the solutes occupy substitutional sites where the substitution of some *n*-paraffin molecules for aromatic molecules, the so-called "key and hole rule", occurs. The high degree of orientation of the solute molecules was deduced by Lamotte and Joussot-Dubien[14] as a result of the observation that the absorption, fluorescence, and phosphorescence spectra of coronene, perylene, and pyrene in *n*-heptane are dichroic in character. Also, by using X-ray diffraction and electron spin resonance techniques, Merle and co-workers[15] elegantly demonstrated that when coronene molecules are frozen in *n*-heptane matrix they occupy principally substituted sites through the replacement of three alkane chains by the solute. Although different sites can be created, the occupation of an identical site by the solute (the solute embedment in an equal molecular field) results in a behavior similar to that of an isolated molecule. The "key and hole rule" proposed by Pfister[12,13] was recently reexamined by Dekkers and co-workers.[16] They concluded that with naphthalene, anthracene, and naphthacene in several *n*-alkanes, the rate of freezing and concentration are the critical parameters involved and the "key and hole rule" was not obeyed in these cases.

The rate of freezing undoubtedly plays an important role;[16-20] with a fast freezing rate it is even possible to observe quasi-line spectra with molecules in inappropriate matrix. On the contrary, slow freezing can result in aggregation (such as microcrystalline aggregates) of the solute molecules which produces a broad spectrum. In order to avoid such a problem, Gurov[20] recommended the use of a very fast freezing rate in analytical chemistry.

The quasi-linear spectra also depend on the concentration range,[21-23] and the phenomenon seems to be related to the solute-matrix compatibility. An excellent review of this and other related problems was written by Ruziewicz.[23]

Another interesting question on the quasi-linear spectra is the appearance of a multiplet structure which has been largely examined,[7-10,24] and it has been established that one of the principal reasons for its appearance is the presence of several different orientations of the solute molecules in the solidified *n*-paraffin (different sites); when broad excitation is utilized, the emission spectra are in consequence called "multiple site spectra".[9] On the contrary, excitation of a specific site (using laser excitation) results in the appearance of a much simpler spectrum.

Besides freezing rate, the quasi-linear effect is extremely sensitive to variation in temperature, as will be seen in this review. An interesting theoretical interpretation was that of Rebane and Khizhnyakov,[25] who suggested that the quasi-linear spectra at low temperatures were the optical analogs of the Mössbauer lines; as such, a single site emission — more easily observed at 4.2 K — should be a zero-phonon line, which is usually accompanied by a "phonon wing".[26] The phonon wing is the result of the electronic transition accompanied by changes in the lattice vibrational state. The temperature decrease (<20 K) also resulted, in some cases, in the observation of Shpol'skii effect in compounds with which the quasi-linear spectra were not observed at 77 K. A study by Richard and Rice[27] led to the conclusion that solute-lattice coupling parameters of several PAHs in frozen *n*-paraffins are indeed small and similar to the values found with f-electrons excitation in organic systems (rare earth). This small coupling, as a result, leads to the appearance of quasi-lines (zero-phonon lines).

Further studies related to the fundamental aspects of the Shpol'skii effect continue to appear in the literature. However, a comprehensive review and discussion of these aspects is not the objective of the present review.*

II. ANALYTICAL DEVELOPMENT

A. Earlier Applications

1. Qualitative Applications

Since the first work published by Shpol'skii and co-workers in 1952, an increased number of papers have appeared in the literature, most of them devoted to the understanding of the phenomenon. The fundamental works published by Bowen and Brocklehurst[28,29] and Sidman[30] in 1954 to 1955 (working at the University of Oxford and the University of California, respectively) confirmed the existence of the Shpol'skii effect and studied it further, suggesting the existence of a relationship between the size of the emitting molecule and of the solvent molecules for the appearance of the quasi-linear spectra,[28,29] or employing the effect to determine vibrational levels in the molecule of coronene.[30] Bowen and Brocklehurst[28,29] also showed that by selective excitation the detection of coronene (Co) or benzo[ghi]perylene (B[ghi]Pe) in the presence of each other is possible. The possibility of detecting the contamination of B[ghi]Pe in Co appeared.

---

* An up-to-date review of the fundamental aspects of the Shpol'skii effect was made recently.[130]

Due to the characteristic aspect of the photoluminescent spectra obtained using the Shpol'skii effect, its qualitative application started soon; in 1959 Dikun and co-workers[31-33] (at the Laboratory of Experimental Oncology, Institute of Oncology, Leningrad) examined the Shpol'skii effect for qualitative purposes and recommended the method for the identification of the well-known carcinogenic compound benzo[a]pyrene (B[a]P) — which had been previously examined from the point of view of vibrational analysis by Shpol'skii and Girdzhiyauskaite[34] — in samples of diverse origin such as food products, polluted air, tobacco smoke, shale tar, etc.[31-33]

Also, the same author identified benzo[e]pyrene (B[e]P), B[a]P, perylene (Pe), B[ghi]Pe, and dibenzo[aj]anthracene (DB[aj]A) in smoked fish[35] and polluted air.[36] Indeno[1,2,3-cd]pyrene (I[1,2,3,-cd]P), dibenzo[ae]pyrene (DB[ae]P), and dibenzo[ai]pyrene (DB[ai]P)[36,37] were also identified in polluted air. Earlier the possibility of distinguishing very similar derivatives such as monomethyl derivatives of benzo[a]anthracene (B[a]A), had been very well demonstrated by Dikun,[38] who concluded that "the fine structure (exhibited) is a reliable criteria for the unambiguous identification of these compounds". Gurov and Novikov,[39] using *n*-hexane as a solvent at 77 K, identified anthracene (A), pyrene (P), B[ghi]Pe, Pe, and Co in soil and snow samples. Florovskaya and co-workers[40-42] identified B[a]P, B[ghi]Pe, and other PAHs in rocks, minerals, and even in carbonaceous chondrite (meteorites).

Parker and Hatchard,[43] using *n*-octane:cyclohexane as a solvent system, were able to investigate an unusual photoreaction of B[a]P in a polymer solution, when the photoproducts (four compounds) were readily distinguished from B[a]P through the quasi-linear spectra.

Lavalette et al.[44] were the first group to apply selective excitation using an excitation monochromator and a 900-W xenon lamp together with quasi-linear luminescence to study the spectral characteristics of seven PAHs such as B[a]A, dibenzo[ah]anthracene (DB[ah]A), P, B[a]P, DB[ai]P, dibenzo[ah]pyrene (DB[ah]P), and benzo[b]fluoranthene (B[b]Ft) (most of which presented carcinogenic action) isolated or in a mixture. It was shown that the selectivity obtained allowed a determination of B[a]P in the presence of B[b]Ft which has a quasi-linear peak (397.6 nm) near the B[a]P strongest emission (at 403.0 nm).[44]

2. *Quantitative Applications*

Apparently, the first quantitative application (semiquantitative) using quasi-linear fluorescence emission was achieved by Bogomolov et al.[45] when a semiquantitative method for the analysis of B[a]P (in *n*-hexane at 77 K), based on the number of lines present in the spectrum, was established; with 1.10^2 μg mℓ^{-1} 21 lines were visible, while only 4 lines were observed at a concentration of 1.10^{-2} μg mℓ^{-1} (10 ng mℓ^{-1}). Il'ina and Personov[46] proposed a method for the determination of Pe in an aromatic fraction of oils and bitumens. The determination was carried out through the estimation of the content of Pe in the samples by comparison with the fluorescence spectrum of an artificial mixture made up of a similar oil with a known concentration of Pe added.

Muel and Lacroix,[47] working at the Laboratoire Pasteur (Institut de Radium, Paris), described the first quantitative method of analysis for B[a]P (at 83 K) in *n*-octane, when the use of the standard addition procedure, usually employed in flame photometry, was proposed. Using the method, Muel and Lacroix[47] obtained a precision of ±10% and a detection limit ("limite de sensibilitê") of ca. 0.1 ng mℓ^{-1}. The method of standard addition was used to avoid variations due to self-absorption, the effect of foreign ions or molecules, and the variation of intensity due to change in the freezing rate. In this excellent work, practical application was also examined.

This was soon followed by Dikun,[48] who in 1961 devised a method for determining B[a]P at 77 K using B[ghi]Pe as an internal standard and *n*-hexane as a matrix. The proportionality between the lines was only observed at low concentrations (less than 4×10^{-6} *M* or ≈1 μg mℓ$^{-1}$), and the relative error for 15 analyses was ±8%. The method was compared with an absorption spectrophotometric method and a sensible improvement in sensitivity (ca. 100 times) was observed with the new method. The author also observed that the presence of B[ghi]Pe, which is usually present in the same chromatographic fraction, did not interfere, as normally occurs in the absorption method.

Personov[49] independently devised a similar internal standard method in *n*-octane at 77 K. A, P, Pe, B[ghi]Pe, and Co were tested as internal standards; Pe and Co gave a fairly sharp fluorescence. Pe, however, has a large number of intensive absorption bands which distort the corresponding part of the fluorescence spectrum of B[a]P, in consequence, Co was used as an internal standard. Personov[49] also observed that the intensity ratio ($I_{B[a]P}/I_{Co}$) was extremely sensitive to changes in the freezing rate; also, if the sample had fluorescence quenchers which modified the intensities of B[a]P and Co in different ways, this was observed to lead to changes in the relative intensity of their lines. Using the method of internal standard, Prokhorova and Znamensky[50] found a concentration of 2.6 ng mℓ$^{-1}$ of B[a]P in paraffin. The progress and difficulties associated with the analytical application of the Shpol'skii effect were described in 1962 by Shpol'skii and Personov.[51]

Eichhoff and Köhler[52] investigated the luminescence characteristics of A, DB[ah]A, 3-methylcholanthrene (3-M-Cho), and B[a]P at 79 K in *n*-heptane; with the latter, the curve of intensity vs. concentration was obtained. The relative error was 6.4% at a concentration of 1 μg mℓ$^{-1}$; the detection limit was 0.67 ng mℓ$^{-1}$.

Personov and Teplitskaya,[53] using the absolute intensity method and the method of additions, determined B[a]P, Pe, and B[ghi]Pe in organic material from minerals and rocks. Using a real sample, a comparison was made between the direct method and the method of standard additions and very similar results were obtained for both Pe and B[ghi]Pe.

Personov and Teplitskaya,[53] however, raise the point that if the sample is known not to quench the fluorescence and strict requirements are not imposed on the magnitude of the error, the analysis can be, in such a case, carried out using the method of comparison with a standard solution rather than by the means of the more accurate method of standard additions.

Jäger and Lugrová,[55] after examining synthetic mixtures, also showed that the amount of B[a]P found after analysis was always less than the amount added (−7 to −10%). The authors explain this effect as being caused by interference from the other compounds present in the mixture. Also it was found that the high concentration limit for B[a]P analysis was 0.15 μg mℓ$^{-1}$ in the final solution, being optimum at a (typical) value of 50 ng mℓ$^{-1}$ (ca. 2×10^{-7} *M*).[55]

Danil'tseva and Khesina[61] established a method for the analysis of 7,12-dimethylbenzo[a]anthracene (7,12-DM-B[a]A) in *n*-octane at 77 K. The method proposed was a combination of both standard addition and internal standard (the combined method); 3,4,5,6,7-tri-benzopyrene (TBP) was chosen as the internal standard as this compound has a sharp quasi-linear fluorescence spectrum in *n*-octane and consequently does not distort the analyte quasi-linear emission.

Dikun et al.[62] compared the combined method described above with the internal standard method and the method of additions for the analysis of B[a]P in *n*-octane at 77 K. As a standard for the internal and combined methods B[ghi]Pe was used. This comparison showed that a large spread in the results was obtained when the method of additions was used (±29%) and similar results (8 to 10%) were obtained when either the internal standard or the combined method was employed.

Dikun and co-workers,[62] however, raise the point that when real samples are being analyzed it is possible that they include other substances that might quench the fluorescence signal of the compound being studied. According to Personov and Teplitskaya[53] such compounds — although they present no real problem in either the combined method or in the method of additions — can interfere in the internal standard method. Assays of B[a]P by Dikun and co-workers,[62] in different samples using the internal standard or the combined method, show that the results exhibit discrepancies, but it was not possible to come to the definite conclusion that the impurities present in the samples were responsible for the difference; these workers concluded that the danger from quenching agents in the internal standard method appears to have been greatly overestimated by Personov and Teplitskaya.[53]

Fedoseeva and Khesina[63] investigated the conditions for the quantitative analysis of the eight PAHs using the combined method (standard addition and internal standard method).[61] B[ghi]Pe was used as internal standard when the methods of analysis for 7,12-DM-B[a]A, B[a]A, B[a]P, P, and Pe were established; B[a]P was used as internal standard for the establishment of the method of analysis for DB[ah]A, B[e]P, and B[ghi]Pe. An investigation was also made by these workers using all possible paired combinations of the substances in synthetic mixtures, using a molar ratio of 1:1 (interference:analyte) and a concentration of 100 ng $m\ell^{-1}$ (except Pe which was 10 ng $m\ell^{-1}$) and, in these cases, the maximum error did not exceed 10%.

Biological applications using quasi-linear luminescence have been described by Fedoseeva and Khesina[63] to follow the oxidation of carcinogenic hydrocarbons by bacteria and yeast and also the effect of soil microflora in the destruction of B[a]P.

Table 1 shows most of the earlier and recent applications of the quasi-linear method for the detection or determination of several compounds in diverse samples.

B. Recent Applications

1. Polycyclic Aromatic Hydrocarbons

Although the application of the Shpol'skii effect in the analytical field received earlier attention from groups in Western Europe, some impediments hindered the widespread utilization of this method in the past which seem to be related to the difficulties encountered in the quantitative application, described in this review, and also to the availability of a commercial instrument. Despite that, during the last 10 years a crescent of interest is visible among research groups outside Eastern Europe and, in consequence, interesting contributions relating to the analytical applications using "real" samples, fundamental analytical studies, or instrumental improvements have been made.

In 1972, Lukasiewicz and Winefordner[70] described the effect and enumerated the qualitative advantages and the quantitative problems associated with it. Kirkbright and de Lima[71,72] reviewed the technique and after examining 23 PAHs (including DB[ae]P, dibenzo[al]pyrene (DB[al]P), DB[ah]P, DB[ai]P, 3-methyl-pyrene (3-Me-P), 4,9-di-*tert*-butylpyrene (4,9-D-*t*-BuP), 3,5,8,10-tetraisopropylpyrene (3,5,8,10-TiPrP), benzo[a]naphtho[8,1,2,-cde]naphthacene, etc.) the qualitative characteristic aspect of the quasi-linear spectra and the solvent (matrix) effect were confirmed (Figures 1 and 2). Quantitative aspects also were examined, and Danil'tseva and Khesina's combined method[61] was proposed as a method for the determination of some dibenzopyrenes, using as matrix *n*-octane-cyclohexane (9:1, v/v) at 77 K. In this matrix, however, DB[ah]P does not show quasi-linear luminescence. In such studies with dibenzopyrenes, the quenching effect by other PAHs was observed. High limits of detection were found in most of the cases, which can be attributed to the low excitation source power (50 W, mercury discharge lamp) utilized. A synthetic mixture of eight PAHs (P, B[a]A, 3-M-Cho, DB[ah]A, DB[al]P, B[a]P, DB[ah]P, and DB[ai]P) was examined. Although some overlap occurs in certain cases, the presence of other peaks permits the identification. In the search for new Shpol'skii solvents, tetrahydrofuran (THF) showed good

Table 1
COMPOUNDS IDENTIFIED OR DETERMINED IN "REAL" SAMPLES USING QUASI-LINEAR METHOD

Compound	Sample	Method[a]	Ref.
Anthanthrene	Air	ident.	81
	Car exhaust	s.a.	56
		ident.	81, 82
	Medicinal oils	ident.	95
Anthracene	Medicinal oils	ident.	95
	Fuel oil	ident.	105[b]
	Particulates	ident.	105[b]
	Shale oil	ident.	105[b]
	Soil	ident.	39
	Snow	ident.	39
	Tarry residue	ident.	105[b]
9,10-Dimethyl anthracene	Coal	ident.	86
Benzo[a]anthracene	Car exhaust	c.m./s.a.	79
		ident.	82, 85
	Coal	ident.	110[b]
	Coal liquid	ident.	105[b]
	Heating system soot	c.m./s.a.	79
	Industrial effluents	c.m.	65
	Medicinal oils	ident.	95
	Petroleum pyrolysis products	ident.	87
	Tarry residue	ident.	105[b]
	Waste water	c.m.	66
Dibenzo[ac]anthracene	Industrial effluents	c.m.	65
Dibenzo[ah]anthracene	Car exhaust	c.m./s.a.	79
	Industrial effluents	c.m.	65
	Particulates	ident.	105[b]
	Petroleum pyrolysis products	ident.	87
	Tarry residue	ident.	105[b]
	Waste water	c.m.	66
Dibenzo[aj]anthracene	Air	ident.	36
	Smoked fish	ident.	35
Chrysene	Car exhaust	c.m.	66, 79
	Coal	ident.	86
	Coal liquid	ident.	105[b]
	Crude oil	ident.	96
	Fuel oil	ident.	105[b]
	Heating system soot	c.m.	66, 79
	Medicinal oils	ident.	95
	Naphthalene (technical)	c.m.	101
	Particulates	ident.	105[b]
	Shale oil	ident.	105[b]
	Tarry residue	ident.	105[b]
Chrysene-a	Sediments	ident.	94
Methylchrysenes	Crude oil	ident.	96
Coronene	Air	ident.	81
	Alumina plant emissions	ident.	81
	Car exhaust	ident.	81, 82
		c.m./s.a.	79
	Coal/coal tar	ident.	86
	Heating system soot	c.m./s.a.	79
	Particulates	ident.	105[b]
	Petroleum pyrolysis products	ident.	87

Table 1 (continued)
COMPOUNDS IDENTIFIED OR DETERMINED IN "REAL" SAMPLES USING QUASI-LINEAR METHOD

Compound	Sample	Method[a]	Ref.
	Pitch extract	ident.	86
	Snow	ident.	39
	Soil	ident.	39
	Waste water	c.m.	66
Fluoranthene	Car exhaust	c.m./s.a.	79
	Coal liquid	ident.	105[b]
	Fuel oil	ident.	105[b]
	Heating system soot	c.m./s.a.	79
	Medicinal oils	ident.	95
	Naphthalene	c.m.	101
	Particulates	ident.	105[b]
	Sediment	d.c.	84
	Shale oil	ident.	105[b]
	Tarry residue	ident.	105[b]
	Water	d.c.	84
Benzo[b]fluoranthene	Car exhaust	c.m./s.a.	79
	Coal tar	ident.	86
	Heating system soot	c.m./s.a.	79
	Medicinal oils	ident.	95
	Pitch extract	ident.	86
	Sediment	d.c.	84
	Water	d.c.	84
Benzo[k]fluoranthene	Car exhaust	ident.	82
	Coal liquid	ident.	121[c]
	Medicinal oils	ident.	95
	Particulates	i.s.	124[c]
	Petroleum pyrolysis products	ident.	87
Indole	Naphthalene	c.m.	101
3-Methylcholanthrene	Coal liquid	ident.	105[b]
Perylene	Air	ident.	36
	Car exhaust	c.m./s.a.	79
	Coal/coal tar	ident.	86, 110[b]
	Coal liquid	ident.	105[b]
	Fuel oil	ident.	105[b]
	Heating system soot	c.m./s.a.	79
	Liquid fuels	i.s.	123[c]
	Medicinal oils	ident.	95
	Mineral/rocks	d.c./s.a.	53, 60
	Oils and bitumens	d.c.	46
	Particulates	ident.	105[b]
	Pitch extract	ident.	86
	Shale oil	ident.	105[b]
	Smoked fish	ident.	35
	Snow	ident.	39
	Soil	ident.	39
	Tarry residue	ident.	105[b]
	Waste water	c.m.	66
Benzo[ghi]perylene	Air	ident.	36, 81
	Alumina plant emissions	ident.	80, 81
	Car exhaust	ident.	81, 82
		s.a.	56
		c.m./s.a.	79
	Coal/coal tar	ident.	86, 110[b]
	Coal liquid	ident.	105[b]
	Coronene	ident.	59

Table 1 (continued)
COMPOUNDS IDENTIFIED OR DETERMINED IN "REAL" SAMPLES USING QUASI-LINEAR METHOD

Compound	Sample	Method[a]	Ref.
	Heating system soot	c.m./s.a.	79
	Industrial effluents	c.m.	65
	Medicinal oil	ident.	75
	Meteorites	ident.	42
	Mineral/rocks	d.c./s.a.	53, 60
		ident.	40—42
	Particulates	ident.	105[b]
		i.s.	124[c]
	Petroleum pyrolisis products	ident.	87
	Pitch extract	ident.	86
	River sediment	d.c.	84
	River water	d.c.	84
	Smoked fish	ident.	35
	Snow	ident.	39
	Soil	ident.	39
	Tarry residue	ident.	105[b]
	Waste water	c.m.	79
Phenanthrene	Car exhaust	c.m./s.a.	79
	Coal	ident.	110[b]
	Coal liquid	ident.	105[b]
	Crude oil	ident.	96
	Fuel oil	ident.	105[b]
	Heating system soot	c.m./s.a.	79
	Naphthalene	c.m.	101
	Particulates	ident.	105[b]
	Shale oil	ident.	105[b]
	Tarry residue	ident.	105[b]
Methylphenanthrenes	Geochemical samples	ident.	88, 89, 93, 96
		c.m.	90
Ovalene	Coal extract	ident.	86
	Pitch extract	ident.	86
Pyrene	Car exhaust	c.m./s.a.	79
		ident.	80, 82
	Coal liquid	s.a.	77[c], 121[c], 122[c]
	Crude oil	ident.	96
	Fuel oil	ident.	105[b]
	Heat transfer oil	ident.	125[c]
	Heating system soot	c.m./s.a.	79
	Medicinal oils	ident.	95
	Petroleum pyrolysis products	ident.	87
	Pitch extract	s.a.	121[c]
	Shale oil	ident.	86, 105[b]
	Soil	ident.	39
	Snow	ident.	39
	Tarry residue	ident.	105[b]
	Waste water	c.m.	66
1-Methylpyrene	Air	ident.	81
	Car exhaust	ident.	81, 82
	Crude oil	ident.	96
	Heat transfer oil	ident.	125[c]
	Petroleum pyrolysis products	ident.	87

Table 1 (continued)
COMPOUNDS IDENTIFIED OR DETERMINED IN "REAL" SAMPLES USING QUASI-LINEAR METHOD

Compound	Sample	Method[a]	Ref.
2-Methylpyrene	Crude oil	ident.	96
3-Methylpyrene	Heat transfer oil	ident.	125[c]
4-Methylpyrene	Air	ident.	81
	Car exhaust	ident.	81, 82
	Coal liquid	ident.	121[c]
	Crude oil	ident.	96
	Heat transfer oil	ident.	96
	Petroleum pyrolysis products	ident.	87
Benzo[a]pyrene	Air	ident.	31, 33, 36, 81
		d.c.	52
	Aircraft exhaust	s.a.	67
	Alumina plant emissions	ident.	81
	Car exhaust	ident.	80, 82
		s.a.	55
		c.m./s.a.	79
	Carbon black	i.s.	49
	Coal/coal tar	ident.	86, 110[b]
	Coal liquid	s.a.	77[c], 121[c] 122[c]
		ident.	105[b]
	Coke industry	ident.	68
	Cooling fluid	ident.	69
	Diesel motor exhaust	s.a.	54
	Drinking water	s.a.	47, 57, 58
		d.c.	83, 84
	Food	ident.	31, 33
	Greases	ident.	59
	Heating system soot	c.m./s.a.	79
	Industrial effluents	c.m.	65, 68, 69
	Industrial oils	c.m.	64, 69
	Liquid fuels	s.a./i.s.	123[c]
	Machine oil	ident.	69
	Medicinal oil	ident.	95
	Meteorites	ident.	42
	Mineral/rocks	d.c./s.a.	53
		ident.	40, 42
	Paraffin oil	i.s.	50, 69
	Particulates	i.s.	124[c]
		ident.	105[b]
	Petroleum	ident.	69
	Petroleum pyrolysis products	ident.	87
	Pitch extract	ident.	86
	Rain water	s.a.	83
	River sediments	d.c.	84
	River water	s.a.	83
		d.c.	84
	Shale oil	s.a.	121[c]
		ident.	105[b]
	Shale tar	ident.	31, 33
	Smoked fish	ident.	35
	Snow	s.a.	67

Table 1 (continued)
COMPOUNDS IDENTIFIED OR DETERMINED IN "REAL" SAMPLES USING QUASI-LINEAR METHOD

Compound	Sample	Method[a]	Ref.
	Soil	s.a.	67
	Spirits	s.a.	47
	Tarry residue	ident.	105[b]
	Tobacco smoke	ident.	31—33
		s.a.	47
Benzo[e]pyrene	Car exhaust	ident.	82
		c.m./s.a.	79
	Coal	ident.	110[b]
	Coal liquid	s.a.	121[c]
		ident.	105[b]
	Heating system soot	c.m./s.a.	79
	Heat transfer oil	ident.	125[c]
	Fuel oil	ident.	105[b]
	Particulates	ident.	105[b]
	Petroleum pyrolysis products	ident.	87
	Shale oil	ident.	105[b]
	Smoked fish	ident.	35
	Tarry residue	ident.	105[b]
	Waste water	c.m.	66
Dibenzo[ae]pyrene	Air	ident.	36, 37
Dibenzo[ah]pyrene	Coal	ident.	86, 110[b]
	Pitch extract	ident.	86
	Tarry residue	ident.	105[b]
Dibenzo[ai]pyrene	Air	ident.	36, 37
	Coal	ident.	86
	Coal liquid	ident.	105[b]
	Particulates	ident.	105[b]
	Pitch extract	ident.	86
	Tarry residue	ident.	105[b]
Indeno[1,2,3-cd]pyrene	Air	ident.	36, 37
	Car exhaust	c.m./s.a.	79
	Medicinal oils	ident.	95
Quinoline			
Benzo[h]quinoline	Crude oil	ident.	104
Sulfur derivatives	Carbon black	ident.	103
Tryphenylene	Coal liquid	ident.	105[b]
	Fuel oil	ident.	105[b]
	Particulates	ident.	105[b]
	Shale oil	ident.	105[b]
	Tarry residue	ident.	105[b]

[a] Methods employed: ident. = identification; d.c. = direct comparison using an analytical calibration curve; s.a. = determination using standard addition method; c.m. = determination using combined method (standard addition *plus* internal standard); i.s. = determination using internal standard method.

[b] Using X-ray as excitation source.

[c] Using laser as excitation source.

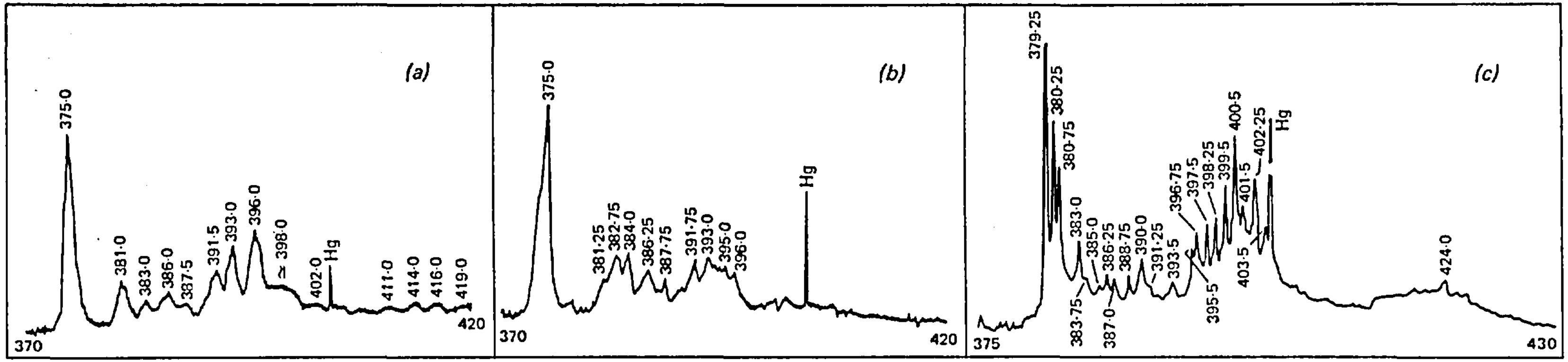

FIGURE 1. Quasi-linear spectra at 77 K, of some alkyl pyrenes in *n*-octane:cyclohexane (90:10, v/v). (a) 3-Methyl pyrene; (b) 3,4-di-*t*-butylpyrene; and (c) 3,5,8,10-tetraisopropylpyrene. (From Kirkbright, G. F. and de Lima, C. G., *Analyst (London)*, 99, 338, 1974. With permission.)

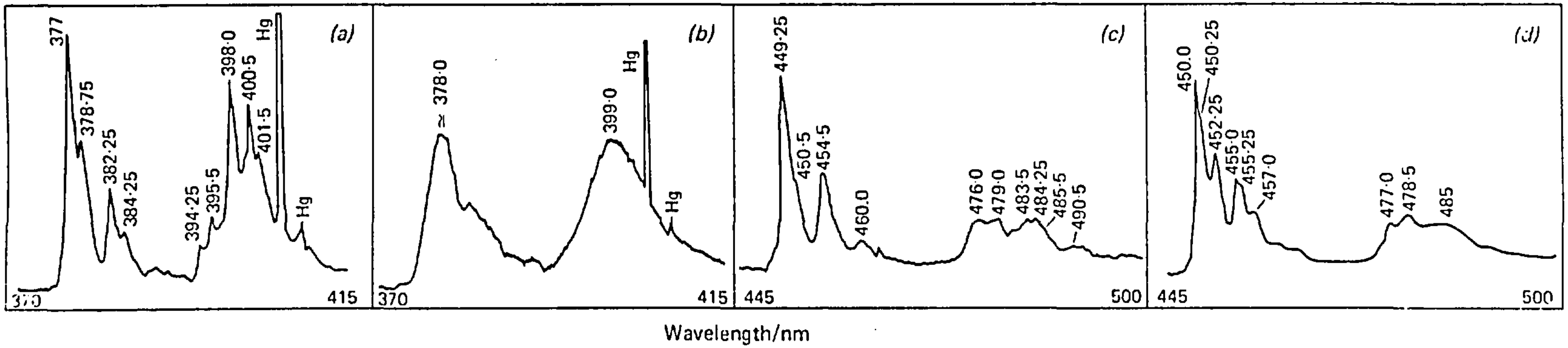

FIGURE 2. Matrix effect on the quasi-linear spectra (at 77 K) of anthracene in (a) *n*-hexane:cyclohexane and (b) in *n*-octane:cyclohexane; and for dibenzo[ah]pyrene in (c) *n*-octane:cyclohexane and (d) *n*-decane:cyclohexane. The ratios between the *n*-paraffin and cyclohexane were constant (90:10, v/v). (From Kirkbright, G. F. and de Lima, C. G., *Analyst (London)*, 99, 338, 1974. With permission.)

results using Co as a model compound.[73] Besides Co, quasi-linear or very narrow band emission was present with 4,9-D-*t*-BuP, dibenzo[ab]anthracene (DB[ab]A), DB[ah]A, B[ghi]Pe, 3-M-Cho, P, B[e]P, DB[ae]P, DB[al]P, ovalene (Ov), and benzo[b]fluorene (B[b]Fl). Drastic reduction of the Co quasi-linear emission appears with the increase of the peroxide content as a result of THF aging.[73]

Gaevaya and Khesina,[74] after examining 15 PAHs — most with recognized carcinogenic action — using either Shpol'skii effect fluorescence (B[a]A, DB[ab]A, P, B[a]P, DB[ai]P, etc. in *n*-octane) or phosphorescence (B[e]P, phenanthrene (Ph), fluoranthene (Ft), chrysene (Ch), and triphenylene (T) in *n*-heptane), proposed the optimum conditions recommended for the quantitative analysis (using the combined method earlier suggested)[61] such as the analyte and internal standard wavelengths and some statistical data. The relative standard deviations (RSD) (10 measurements) were in the range of 2.2 to 9.3% using solutions of the isolated compounds with concentrations of 100 and 1000 ng mℓ^{-1}. A synthetic mixture of the 15 PAHs studied was examined, with a final concentration of 665 ng mℓ^{-1} through the fluorescence and phosphorescence spectra. With the exception of Ph and A, all other compounds were identified in this mixture. In the first case, some quasi-lines of Ph (at 461.6 and 498.1 nm) are overlapped, respectively, by the strong emission of T at 461.8 nm and by Ch at 498.1 nm. On the other hand, spectral interference in the A spectrum is done by dibenzo[al]anthracene (DB[al]A) and B[a]P. In such circumstances Gaevaya and Khesina[74] suggested a previous chromatographic separation. The use of selective excitation in place of the broad band (240- to 400-nm band filter) system employed probably might help to solve the problem of spectral interference. Despite this problem, the authors, using the combined method, found a relative error of 10% in the determination of all individual PAHs (but A and Ph) in the synthetic mixture.

Colmsjö and Stenberg[75] examined the effect of changing the *n*-alkane solvents (from *n*-pentane to *n*-octane) in the quasi-linear fluorescent spectra of 14 PAHs when it was confirmed that the *n*-alkane solvent used has a strong influence in the spectra. The authors proposed as the best Shpol'skii solvent, for the qualitative analysis, the one which produces the largest number of quasi-lines. The effect of the freezing rate in the Co spectrum was also studied, corroborating previous Shpol'skii observations.[9] For such studies, a laboratory-built sample compartment was constructed.

Employing a laboratory-built high-resolution spectrofluorimeter, Winefordner and co-workers,[76] after examining 23 PAHs in different *n*-paraffins (from *n*-pentane to *n*-nonane), selected the best Shpol'skii matrix or matrices as those in which the narrowest bandwidths are observed for such compounds. A table was presented as a result of this work, which is a useful guide in the choice of the best solvent(s) where the narrow band widths are produced. Limits of detection of both emission and excitation of judiciously chosen peaks were also determined. An examination of the quantitative capability of the Shpol'skii effect was also carried out by the same authors. A synthetic mixture of 11 compounds, using *n*-heptane as the solvent (following the suggestion of Yang et al.[77] who found that in *n*-heptane, quasi-linear emission appears with PAHs that have from three- to six-ring structures), was prepared, and the concentration of each component was determined using the combined method.[61] The present error ranged from 1 to 16% and this was attributed to "inhomogeneity in the orientation of the analyte molecules in the matrix, the typical uncertainty observed in the fluorimetric technique and the possibility of the standard addition measurements having been made in the non-linear part of the intensity-concentration curve".[76]

Colmsjö and Stenberg[78] investigated the effect of temperature (from 300 to 63 K) on the quasi-linear spectra of Pe, DB[ah]A, and T using the laboratory-built cell.[75] The cell was, however, modified to decrease the temperature further from the liquid nitrogen temperature of 77 K to 63 K. Although the temperature was stable for only 10 min, the time was sufficient for the scanning of the spectra. The effect of lowering the temperature below 77 K resulted in a further improvement in the resolution, which helps in the identification and determination of the compound and suggests that temperatures lower than 77 K are much more useful.

The association of thin-layer chromatography with quasi-linear luminescence or capillary gas chromatography was used by Khesina and co-workers[79] for the identification and quantitation of several PAHs present in soot from a heating system and in car exhaust gases.

Utilizing vacuum sublimation separations technique together with the Shpol'skii spectroscopy, Colmsjö and Stenberg[80] proposed an interesting method for the identification and determination of some PAHs (P, Co, B[a]P, and B[ghi]Pe). The PAH compounds were sublimated straight from a cut-out section of the thin-layer plates (coated with 30% acetylated cellulose) to a cold-finger.

The association of quasi-linear emission, after a previous separation of PAHs using reversed-phase high performance liquid chromatography (RPHPLC), was examined by Colmsjö and Stenberg[81] with samples of automobile exhaust, air (from Stockholm), and from emissions of an alumina reduction plant. From the quasi-linear spectra obtained with the fractions, the authors identified 1-methylpyrene, (1-Me-P), 4-methylpyrene (4-Me-P), B[ghi]Pe, anthanthrene (An), and Co (Figure 3) in automobile exhaust and in the Stockholm environment air. In the particulate emission from an alumina reduction plant, B[a]P, P, B[ghi]Pe, and Co were identified.

Further details in the application of the Shpol'skii effect technique for the identification of PAH in RPHPLC fractions were also described by the same authors in the Third International Symposium on Chemistry and Biology of PAH.[82] The examination of particulate from automobile exhaust gases after a clean-up procedure and HPLC separation (using a UV-detector system) led to the identification of 1-Me-P, P, B[a]A, B[e]P, benzo[k]fluoranthene (B[k]Ft), B[ghi]Pe, Co, and An. Once again, the extraordinary capability in the identification of PAHs was demonstrated by the Shpol'skii method.[82]

Liquid-liquid extraction was used in conjunction with the Shpol'skii method by Monarca et al.[83] for the proposal of a quick routine method for the determination of B[a]P in water samples (either river, rain, or drinking water).

Interference effect studies in the B[a]P signal were also carried out using synthetic mixtures of this compound with I[1,2,3,-cd]P, Ft, and B[k]Ft with ratios which are usually found in "real" water samples; only at a B[a]P concentration of 1.10^{-6} *M* was a 20% decrease in the signal observed.

Following the same line, Santoni and Mandon[84] established a procedure for the determination of five PAHs (B[a]P, Ft, B[b]Ft, B[ghi]Pe, and I[1,2,3,-cd]P), which were recommended by the W.H.O. and E.C.C. as pollution indicators, in water and river sediments (Shpol'skii matrix *n*-octane was used at a temperature of 77 K). Although this solvent is inappropriate for Ft and as a consequence a very broad spectrum appeared (with a bandwidth of 500 cm^{-1}), the authors concluded that the simultaneous identification of all six PAHs in the samples was possible.

Paturel et al.[85] also examined these six PAHs together with P, B[e]P, benzo[j]fluoranthene (B[j]Ft), and benzo[b]chrysene (B[b]Ch) using a special laboratory-constructed cell compartment, at 10 K, and as matrix *n*-octane. Even at this low temperature, Ft did not display the characteristic Shpol'skii bandwidth due, again, to the inappropriate matrix employed. Very narrow bandwidths (0.1 nm) were observed with other compounds. A mixture of these ten compounds was examined and in such circumstances the presence of B[k]Ft (with an emission at 403.40 nm) was perfectly detected in the vicinity of a strong emission of B[a]P (in 402.95 nm).

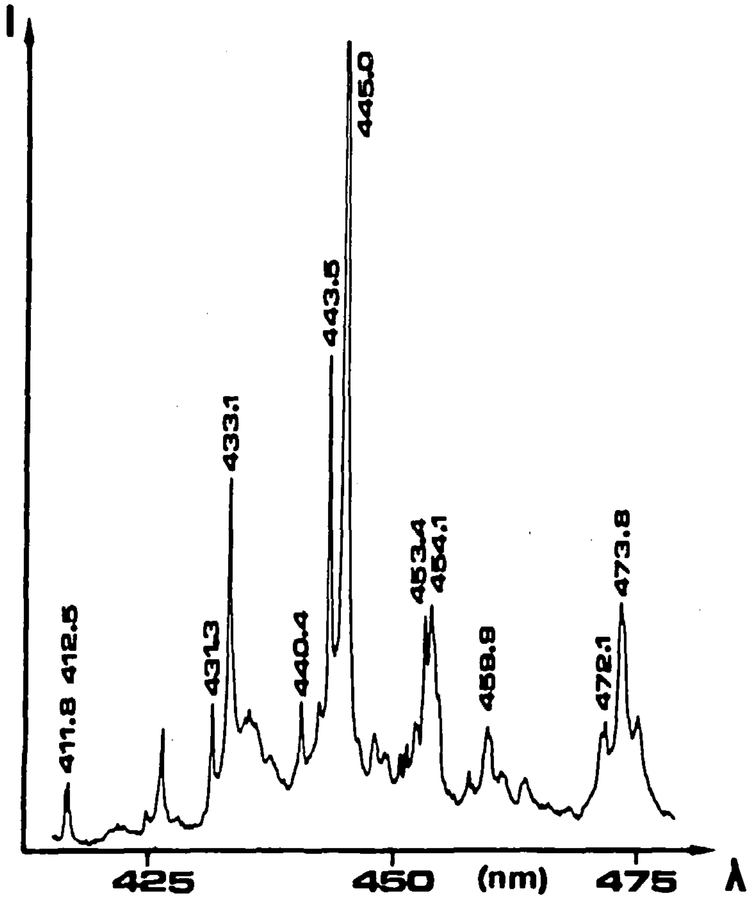

FIGURE 3. Quasi-linear spectrum of coronene identified in a chromatographic fraction from an automobile exhaust extract. (Reprinted with permission from Colmsjö, A. and Stenberg, U., *Anal. Chem.*, 51, 145, 1979. Copyright 1979 American Chemical Society.)

Twelve PAHs have been identified in coal and coal tar pitch extracts using Shpol'skii luminescence at 77 K by Drake et al.[86] In this case, the method showed it was capable of detecting several PAHs without a previous laborious clean-up and separation procedure.

In another paper, Colmsjö and Östman[87] compared the Shpol'skii effect methodology with glass capillary gas chromatography (using flame ionization detection) after RPHPLC in the analysis of "real" samples. The capability of observing Shpol'skii spectra of PAH compounds in the presence of a broad band fluorescent compound (detected at room temperature using a low resolution instrument) was demonstrated when a fraction with 93% of benzonaphthothiophene — a fluorescent compound detected by mass spectroscopy (MS) and determined by gas chromatography (GC) — showed, in Shpol'skii conditions, the unequivocal presence of 4-Me-P.

The application of the Shpol'skii effect to analytical problems in organic geochemistry and some fundamental aspects related to its application in quantitative analysis has been carried out extensively by Ewald, Garrigues, Lamotte, Joussot-Dubien, Merle, and co-workers, using a laboratory-assembled high-resolution spectrofluorimeter,[88-91,93,94,96] and with this instrumental assembly, selective excitation was possible. The utility of lowering the temperature below 77 K was examined by these workers

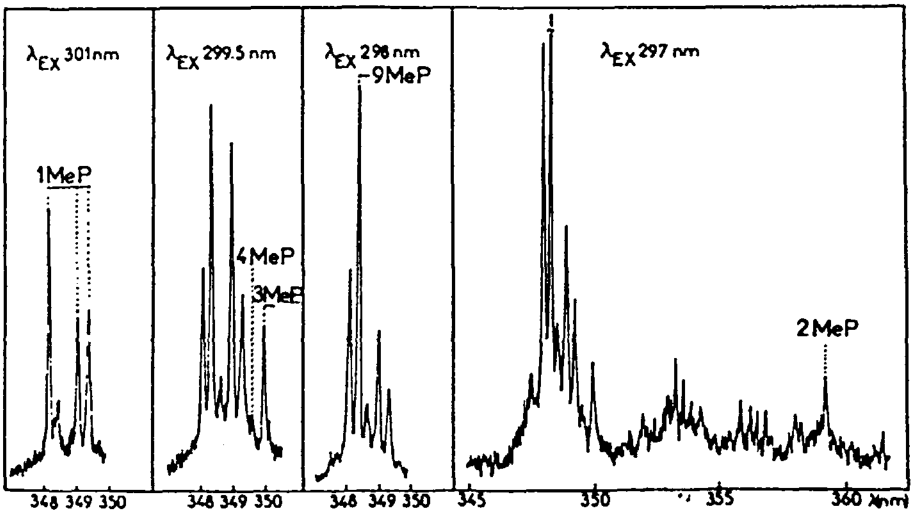

FIGURE 4. Selective excited fluorescence spectra (0,0 range transition) at 4.2 K of monomethylphenanthrene isomers identified in a petroleum fraction. (Reprinted with permission from Rima, J., Lamotte, M,. and Joussot-Dubien, J., *Anal. Chem.*, 54, 1059, 1982. Copyright 1982 American Chemical Society.)

when a cryogenerator assembly (15 K) and a helium cryostat (4.2 K) were tested.[88] Using the cryogenerator, the authors successfully identified some monomethylphenanthrene isomers (in *n*-hexane) present in a chromatographic fraction (from petroleum samples) either by quasi-linear fluorescence or phosphorescence.

Ewald et al.[89] used high-resolution spectrofluorimetry (HRS) and the Shpol'skii effect joinly with capillary GC-MS techniques for the identification of monomethylphenanthrene isomers in petroleum samples. The authors concluded that the quasi-linear spectrum technique used in conjunction with GC-MS helped in the identification and in the quantitative estimation of the methylphenanthrene compounds present.

Rima et al.,[90] using HRS, investigated further the problems involved in the application of the Shpol'skii effect for the determination of monomethylphenanthrene isomers in a petroleum fraction (Figure 4). According to the authors, quoting previously published papers, Ph and its derivatives are compounds in which the problems associated with the compatibility with the *n*-paraffin crystal lattice and the freezing rate are much more critical. Even at low concentrations, Ph molecules associate in such a manner (called "preaggregates" by the authors) that broad band emission is observed, the association being greater in the presence of A.[91] *n*-Hexane was used as the solvent as the multiplet emission was much simpler than the multiplet observed in *n*-heptane. The authors first used A as internal standard.

By examining the precision of the signal, using 9-methylphenanthrene as analyte in the function of the sample tube position or the freezing rate, the authors observed that the reproducibility of the ratio of the analyte fluorescence intensity over the intensity of the standard was dependent on the multiplet component chosen. This was explained as due to a different dependence of the multiplet upon the cooling rate. In general, the low reproducibility observed was attributed to the inhomogeneous diffuse medium which characterizes the polycrystalline frozen *n*-paraffin solutions, "where the Beer-Lambert law is not perfectly obeyed".[90,92] Better reproducibility was observed with *n*-hexane (±15%) in place of *n*-heptane (±25%).

Quantitative determinations of synthetic mixtures using the standard addition method and A as internal standard showed some discrepancies in the results, which suggested that some kind of energy transfer exchange was happening with the A molecules. Substitution of A as internal standard by acenaphthene resulted in a better accuracy, as all the results were found with positive deviations in the range of 15 to 24%. Despite these difficulties, the authors consider that there is one important advantage which is the certainty obtained (due to the characteristic spectrum) in the determination of such similar isomers. These results let these authors[90] determine five methylphenanthrenes in HPLC fractions isolated from a petroleum sample.

Garrigues et al.[93] compared the Shpol'skii frozen solution method using HRS (at 15 K) with the nitrogen matrix isolation method; much more structured spectra were observed with the former technique. The identification and determination of five monomethylphenanthrenes carried out in North Sea petroleum HPLC fractions using the combined method[61] were compared with the GC-MS method, showing good agreement in the results.

Ewald and co-workers,[94] using a working temperature of 4.2 K, identified some PAHs derived from triterpene (chrysene-a) which are present in geological sediments. The HPLC fraction, when fluorimetrically examined in frozen *n*-heptane, showed a similar spectrum of a standard sample of chrysene-a, demonstrating once more the selective capability of the Shpol'skii effect. Despite the large alkylated part of the molecule (ethylcyclopentene) which makes, according to the authors, the structure not appropriate for a perfect embedment in the crystal lattice (*n*-heptane), quasi-linear spectra were observed[94] when concentrations lower than 1.10^{-6} *M* were used.

Recently a procedure for the detection and determination of PAHs in medicinal white oils was described by Colin et al.,[95] employing a previous three-stage chromatographic procedure followed by HPLC coupled to a fluorescence detector, for detection and determination, and quasi-linear fluorescence spectrometry using HRS and 4.2 K, for the confirmation and identification of the PAHs. The effect of changing the temperature from 77 to 4.2 K was studied, resulting, as expected, in a much better spectral resolution, which is shown in Figure 5.

Garrigues and Ewald[96] expanded further the utility of quasi-linear spectroscopy, applying this technique to the identification of several monomethylated derivatives of P, Ph, and Ch in crude oils. The interest in the identification and possible determination of these compounds is related to the well-known carcinogenic behavior of some of these isomers, which were identified after a previous HPLC separation.

An investigation of the utilization of photoacoustic spectroscopy of PAH using Shpol'skii matrices at 77 K was carried out by the Winefordner group.[97] Although dye laser excitation was employed, the limits of detection were in the range of $\mu g\ m\ell^{-1}$, in contrast with the Shpol'skii fluorimetry which has limits of detection in the range of $ng\ m\ell^{-1}$. Also, the photoacoustic spectra lack the resolution usually found in the quasi-linear spectra.

The merger of the quasi-linear spectroscopy with the synchronous luminescence spectroscopy technique was demonstrated by Inman and Winefordner,[98] employing a laboratory-constructed spectrofluorimeter (and a temperature of 77 K) whose monochromator scan controls were controlled by a microcomputer. Constant energy difference was maintained between the monochromators and the technique was consequently called low temperature constant energy synchronous luminescence spectroscopy (LTCESLS). In comparison with the conventional luminescence spectrometry, LTCESLS showed some advantages such as much narrower spectral bands, the possibility of examining complex mixtures, and the decrease in the Rayleigh and Raman scatter. The application of the technique using a temperature of 4 K in place of 77 K was theoretically examined by the authors.

2. *Other Aromatic Compounds*

Despite the large number of organic compounds studied (besides PAHs) using the

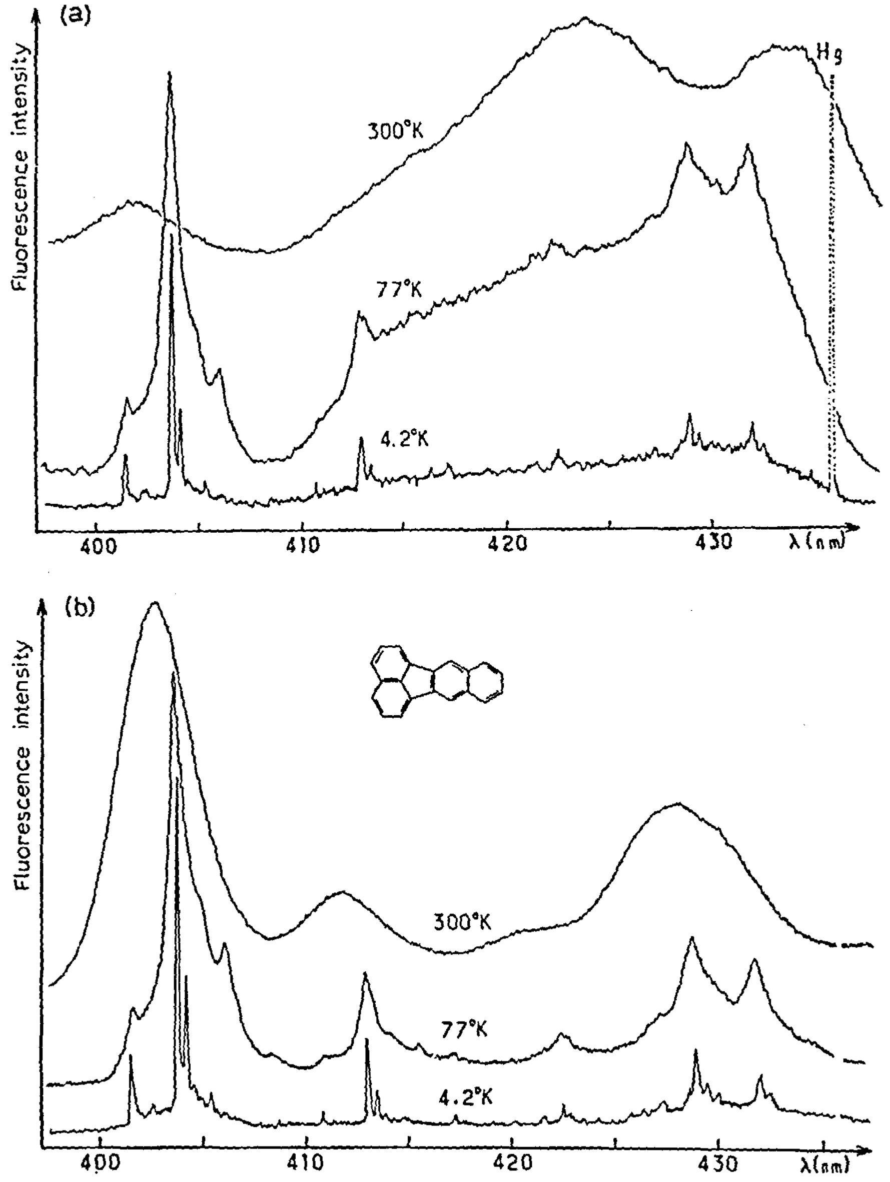

FIGURE 5. Temperature effect in the quasi-linear spectra, in *n*-heptane, of (a) a chromatographic fraction in which B[k]Ft was present and (b) of an authentic sample of B[k]Ft. (From Colin, J. M., Vion, G., Lamotte, M., and Joussot-Dubien, J., *J. Chromatogr.*, 204, 135, 1981. With permission.)

Shpol'skii effect, such as several PAH *N*-heteroanalogs, polyphenyls, diphenylpolyenes, diaryldivinylbenzenes, indigoids, thioindigoids, porphyrins, and phthalocyanines, etc.,[99] there are few analytical applications in the literature with these compounds. This gives us the impression of a fertile analytical area to be examined by analysts. Due to the biological interest of the hydroxy-derivatives of B[a]P, the quasi-linear spectra of two such compounds, 3-hydroxy- and 6-hydroxy-benzo[a]pyrene (3-OH-B[a]P, 6-OH-B[a]P), were studied by Khesina et al.,[100] both from the physicochemical (vibration analysis) and analytical point of view. Using *n*-octane as matrix at 77 K, the authors succeeded in observing quasi-linear fluorescence spectra, although they were, as expected, much broader if compared with B[a]P. The spectra of both compounds were red-shifted, ca. 1000 cm^{-1} in relation to the spectrum of B[a]P. In the analytical studies, the combined method[61] was used. Pe (λ_{max} at 451.1 nm) was employed as an internal standard. The method was successfully applied to the determination of one of the hydroxy derivatives in experiments based on the enzymatic oxidation of B[a]P.

Quasi-linear phosphorescence, which has not been frequently used for analytical purposes, was proposed by Pazhnina and co-workers[101] for the detection and determination of indole (In) and some PAHs (Ft, Ph, and Ch) in technical naphthalene (Nap). It was verified that no significant interference was observed in the phosphorescent In signal, even if the Nap to In concentration ratio was ca. 1000:1. At smaller In concentrations, or in the presence of a critical amount of carbazole, the authors suggest a previous chromatographic separation. For such experiments, the workers employed a xenon lamp coupled to a filter for excitation and a classical rotating slotted-cylinder system to isolate the phosphorescent signal from the excitation beam.

Akhobadze et al.[102] examined the quasi-linear spectra of several thiophene derivatives (such as dibenzothiophene) in the direction of establishing a qualitative method of analysis for such compounds. The authors observed that the phosphorescent intensity was usually more intense in comparison with the fluorescent intensity, except in the higher molecular weight molecules studied (compounds with an A nucleus). The best *n*-paraffin solvents (the solvents where the spectra show finer structure) were also determined by the authors. The characteristic spectra obtained suggested that the method could eventually be used for the identification of thiophene benzologs in "real" samples.

An important advance in the utility of the Shpol'skii effect was made by Colmsjö and co-workers[103] when it was found that quasi-linear spectra are observed with compounds in which a sulfur atom is located at the periposition of a polyaromatic hydrocarbon. Several sulfur derivatives were examined and the resolution obtained was similar to the resolution of the parent compound. In some cases, phosphorescent emissions were also observed (Figure 6). The examination of a sample of carbon black, after HPLC, revealed the presence of 7,8-epithiobenzo[ghi]perylene, 10,11-epithiobenzo[a]pyrene, 1,12-epithiobenzo[e]pyrene, and 1,12-epithiotriphenylene in the fractions isolated.

Using HRS, some methylated benzo[h]quinolines were identified in a triaromatic basic concentrate from a crude oil sample.[104] The relative distribution between isomers found by the quasi-linear spectrofluorimetry agreed with GC (glass capillary column) analysis data.

Two isomeric carbazoles (7-H-dibenzo[cg]carbazole and 13-H-dibenzo[ai]carbazole, which are compounds of biological interest due to their carcinogenic character) were examined using X-ray-excited optical luminescence (XEOL) and *n*-heptane.[105] The luminescence spectra observed have enough differences to characterize each isomer. Also employing XEOL, dibenzothiophene — another carcinogenic compound — was tested in THF, cyclohexane, and *n*-heptane; however, only in the latter solvent was a Shpol'skii-type spectrum observed.[105] It is interesting to observe that when this compound was examined by Colmsjö and Östman using UV excitation, no fluorescence was observed.[106]

C. Instrumentation

1. Sources of Excitation

a. Mercury-Vapor Discharge Lamp

The mercury-vapor discharge lamp has been used in most of the reports previously reviewed; wide band filters, interference filters, or even monochromators were used in conjunction with this source. In the Soviet papers, typical mercury lamps quoted are

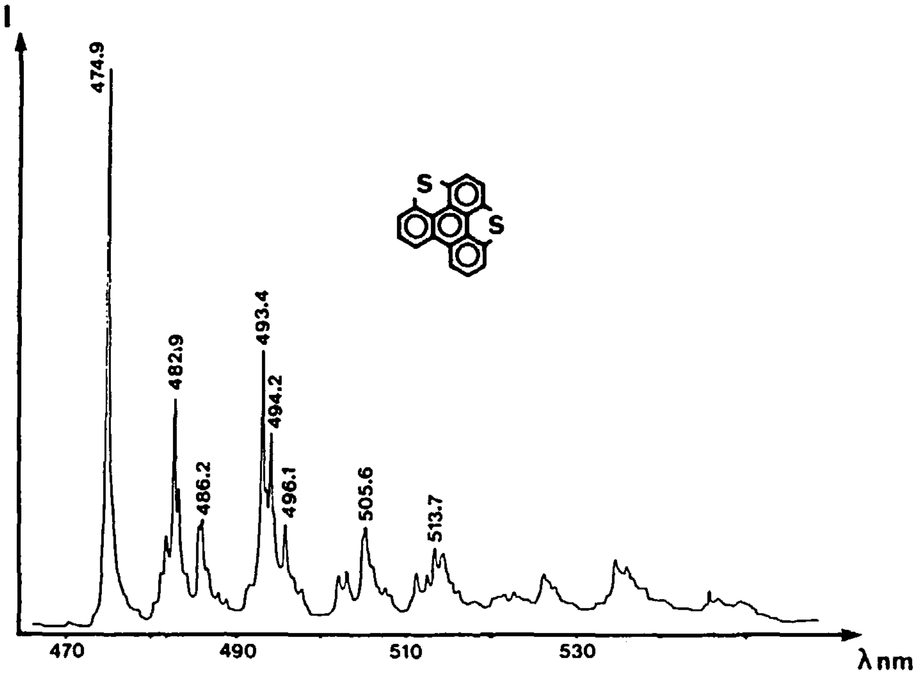

FIGURE 6. Phosphorescent spectrum of 1,12:4,5-epidithiotriphenylene in *n*-hexane. (Reprinted with permission from Colmsjö, A. L., Zebühr, Y. U., and Östman, C. E., *Anal. Chem.*, 54, 1673, 1982. Copyright 1982 American Chemical Society.)

of PRK, DRSh and SVDSh type. The PRK type is of high pressure (ca. 1 atmosphere) and has a quartz envelope; the PRK-2[45,62] (375 W) and PRK-4 (220 W) are some of the types in use. The DRSh (250 or 500 W) type of lamp is also employed; it is a spherical ultra-high-pressure mercury-vapor lamp and was used in combination with a suitable lens and filter.[53-55,60,63,65] Another type of mercury lamp is the SVDSh-250. The SVDSh is a mercury vapor lamp which exhibits a large fraction of its energy in the short wavelength UV region and probably has a power rating of 250 W of power.[55,73,83,108] A 1000-W mercury lamp was recently used by Paturel and co-workers.[85] As expected, the use of a low-power (50 W) lamp resulted in high limits of detection.[71,72]

b. Xenon-Arc Continuum Lamp

In contrast to mercury lamps, those with a xenon source have not been frequently used in the past. Xenon lamps with high power (DKSSh-1000, with 1000 W of power)[107] or a 450-W lamp have been utilized with filters.[74,78,79,82,101] A 150-W xenon lamp has also been examined with interference filters[73,86,108] and more recently with a wide band filter.[84,101] The association of a high-power xenon lamp (900 or 1000 W) with an excitation monochromator was used earlier by Lavalette et al.[44] and Fedoseeva and Khesina;[63] this type of set-up has been used in most of the recent papers in HRS assemblies, the lamp being powered with either 300[97,98] or 450 W.[88-91,93-96,103,104]

Due to the polycrystalline character of the frozen matrix, scattering is a problem in quasi-linear luminescence, principally at high sensitivity settings. Obviously the scatter signal depends on the excitation source employed and the resolution of the dispersive systems employed. Figure 7 shows the typical scatter effect, using an interference filter with the λ_{max} at 300 nm, on the B[a]P quasi-linear emission (in *n*-octane at 77 K) when a mercury discharge lamp or a xenon lamp is employed.[108] The scatter could also produce a direct or partial spectral interference; an example of such a problem is the

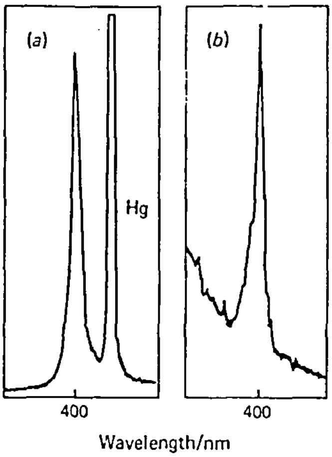

FIGURE 7. Effect of scattered excitation light in the 403.0-nm quasi-linear emission of benzo[a]pyrene (at 77 K, in *n*-octane) using (a) a mercury-vapor discharge lamp and (b) a xenon-arc lamp source. (From Causey, B. S., Kirkbright, G. F., and de Lima, C. G., *Analyst (London)*, 101, 367, 1976. With permission.)

overlap of a strong scatter of 435.8 nm from a mercury-vapor discharge lamp with the weak emission of dibenzofuran in THF at 434.10 nm. Using xenon lamp excitations, however, this problem was solved.[73,108]

c. X-Ray-Excited Shpol'skii Spectra

An interesting development, different from the usual procedure of excitation by UV radiation in the conditions used for the observation of quasi-linear spectra, was obtained by Fassel and co-workers[105,109,110] when X-rays were used instead. In a preliminary work published in 1976, D'Silva et al.[109] described the first observation of the X-ray-excited quasi-linear luminescence of several PAHs (B[a]P, P, B[ghi]Pe, Co, B[a]A, Ph, A, and DB[ah]A) in *n*-heptane at 90 K. Using a tungsten target, which was operated at 50 kV and 40 mA, an X-ray radiation source in the range of 1 to 10 Å was produced and used as an excitation beam. Using this technique called by the authors XEOL, typical Shpol'skii effect spectra were observed. Earlier it was concluded that an obvious advantage of this method was the absence of UV or visible scatter usually present when UV excitation is employed.

In the continuation of this work, Woo et al.[110] applied XEOL for the identification of several PAHs present in coal samples after an extraction and column chromatographic clean-up procedure. In a later paper, Fassel and co-workers[105] examined further the utilization of the XEOL method for the identification and quantitative estimation of some PAHs in particulate samples. In this case, the technique of standard addition was chosen to avoid any distortion caused by "inner filter effects" or energy transfer processes. Also examined in this work were other samples, such as a solvent from a solvent-refined coal process and a condensate from a coal gasification process. Although a previous extraction and column chromatographic technique were utilized, a broad background luminescence was present in the spectrum of the gas stream condensate. As a consequence, these authors[105] suggested that a much more complete clean-up and isolation method would have to be tested in such a case, as this background is believed to be due to the presence of other organic compounds. Despite this problem, several PAHs were identified in these samples. Fuel oil samples were also examined and, in the spectrum obtained, it was possible to identify several PAHs.

d. Laser-Excited Shpol'skii Spectrometry

The information obtained from the work of Shpol'skii and Girdzhiyauskaite[34] and later from Svishchyov[111] showed that a quasi-linear spectrum with full widths at half-maximum in the range of 1 to 10 cm^{-1} is usually also observed in the absorption or excitation mode,[112] suggesting that selectivity will result if a sharp-line excitation system, such as a high-intensity xenon lamp coupled to high-resolution monochromator[44] or, as suggested later as an obvious solution, a laser (preferably a dye laser), is employed. The utilization of a laser in the fundamental studies of the Shpol'skii and related phenomena was made initially by Personov et al.,[113] followed by Vo-Dinh and Wild,[114] Abram et al.,[115] and more recently by Dinse and Winscom.[116] The studies carried out by Personov et al.[113] in conditions where the Shpol'skii effect was not observed (such as Pe in *n*-undecane or in ethanol) called attention to a very interesting effect whose technique is usually referred to as site-selection spectroscopy, selective laser excitation, or fluorescence line narrowing spectroscopy [FLNS]) in which quasi-lines (ca. 1 cm^{-1}) appear after a frozen solution (at a temperature of 4.2 K) is excited by laser radiation. This technique has been pursued by Small and co-workers[117-119] and Bykovskaya et al.[120] during the last few years as another analytical method for the characterization and determination of PAHs and related compounds.

Attempts to use a laser as an excitation source for the determination of PAHs in Shpol'skii conditions were carried out by Causey et al.,[108] when a 7-mW helium-cadmium laser (with emissions at wavelengths of either 325 or 441 nm which could be chosen by a simple changing of mirrors) was examined and compared with a xenon arc (150 W) or a medium pressure mercury-vapor discharge lamp (125 W) interference filter systems. Detection limits obtained with the three excitation systems studied (Table 2) reveal that with the excitation at 325 nm no gain in intensity was obtained with B[a]P if compared with the mercury lamp interference filter system. However, a small gain in the detection limit was observed with Co, B[a]A, and DB[ah]A using the laser (at 325 nm). Pe was better detected when the laser — at 441 nm — was used; this results from the fact that this laser line nearly overlaps the 0,0′ absorption band of Pe which is present at 441.6 nm.[113] It is obvious that this laser source was not completely effective as only two wavelengths were available. The authors concluded that a tunable dye laser source would be beneficial if employed together with the Shpol'skii technique.

Recently, the utilization of a tunable dye laser with the Shpol'skii technique (at 15 K) has been extensively examined by Fassel and co-workers[77,121,124] and described in a series of works, since 1980, when the detection of P, 5-methylpyrene, B[a]P, and B[k]Ft and the quantitation of P and B[a]P (by the method of standard addition, using as a reference another PAH present in the sample) in solvent-refined coal and shale oil was made.[121] The dye laser utilized had a bandwidth of 0.01 to 0.03 nm and the technique was called by Fassel and co-workers laser-excited Shpol'skii spectra (LESS).

In a second work, Yang et al.[77] continued to examine the utilization of LESS in frozen solutions, which is, according to the authors, a much simpler and rapid process for preparing a sample if compared with the matrix isolation technique. In the method used, the sample was first frozen at liquid nitrogen temperature and later cooled down to 15 K. The observation that the multiple site spectra (with nonselective excitation) of B[a]P can be reproduced, even at different concentrations (from 1 ppm to 1 ppb), demonstrated that the cool-down procedure was reproducible, especially if the analyte concentrations are maintained below 1.10^{-6} *M* (ca. 0.25 ppm). The extraordinary advantages of the selective excitation were also shown in this paper when it was demon-

Table 2
[ASI-LINEAR LIMITS OF DETECTION, EXCITATION SYSTEMS, TEMPERATURES, AND ANALYTICALLY USEFUL WAVELENGTHS

Compound	Matrix[a]	ng mℓ^{-1}[b]	Excitation system	Emission wavelength (nm)	Temp. (K)	Ref.
naphtene	nC_5	30 (30)[c]	Xe (300 W) M	318.9	77	76
hracene	nC_6	1.8[d]	L (4 mW) 337.1 nm	402.5	77	125
	nC_7	10	Xe (1000 W) F	386.7	77	74
	nC_7	20 (4)[c]	Xe (300 W) M	380.5	77	76
	$nC_6:cC_6$	50[d]	Hg (50 W) IF	377.0	77	72
·Methylanthracene	nC_8	8 (10)[c]	Xe (300 W) M	387.6	77	76
·Methylanthracene	nC_6	4 (2)[c]	Xe (300 W) M	387.8	77	76
,10-Dimethyl	nC_6	3 (2)[c]	Xe (300 W) M	399.6	77	76
anthracene	$nC_6:cC_6$	50[d]	Hg (50 W) IF	405.75	77	72
,10-Diphenylanthracene	—[e]	20 (10)[c]	Xe (300 W) M	402.7[e]	77	76
enz[a]anthracene	nC_8	0.5[d]	L (3 mW) 325 nm	387.75	77	108
	nC_8	2 (4)[c]	Xe (300 W) M	384.1	77	76
	nC_8	2[d]	Hg (125 W) IF	383.75	77	108
	nC_8	10	Xe (1000 W) F	384.6	77	74
	$nC_8:cC_6$	100[d]	Hg (50 W) IF	383.75	77	72
,12-Dimethyl-benz[a]	$nC_8:cC_6$	3[d]	Hg (125 W) IF	397.75	77	127
anthracene	nC_8	10	Hg (250 W) F	397.20	77	61
	$nC_8:cC_6$	200[d]	Hg (50 W) IF	397.75	77	72
)ibenzo[ac]	nC_8	2 (20)[c]	Xe (300 W) M	374.8	77	76
anthracene	nC_8	10	Xe (1000 W) F	386.2	77	74
)ibenzo[ah]	nC_8	3[d]	L (3 mW) 325 nm	394.25	77	108
anthracene	nC_9	3 (6)[c].	Xe (300 W) M	394.4	77	76
	nC_8	5[d]	Hg (125 W) IF	392.25	77	108
	nC_8	10	Xe (1000 W) F	394.1	77	74
	$nC_8:cC_6$	100[d]	Hg (50 W) IF	394.25	77	72
ızo[a]naphtho ,1,2-cde]naphthacene	$nC_8:cC_6$	300[d]	Hg (50 W) IF	444.75	77	72
·ysene	nC_7	3 (7)[c]	Xe (300 W) M	360.7	77	76
	nC_7	10	Xe (1000 W) F	498.6[f]	77	74
	nC_6	23[d]	L (4 mW) 337.1 nm	379.9	77	125

Table 2 (continued)

SI-LINEAR LIMITS OF DETECTION, EXCITATION SYSTEMS, TEMPERATURES, AND ANALYTICALLY USEFUL WAVELENGTHS

Compound	Matrix[a]	ng mℓ⁻¹ [b]	Excitation system	Emission wavelength (nm)	Temp. (K)	Ref.
enzo[b]chrysene	nC_8	5^g	Hg (1000 W) F	390.20	10	85
onene	nC_6	0.5^d	L (3 mW) 325 nm	445.0	77	108
	nC_6	1^d	Hg (125 W) IF	445.0	77	108
	nC_8	10	Xe (1000 W) F	443.8	77	74
	nC_6	100^d	Hg (50 W) IF	445.0	77	72
oranthene	nC_7	10	Xe (1000 W) F	543.0^f	77	74
	nC_8^e	10	Xe (150 W) F	$—^e$	77	84
	nC_8^e	25^g	Hg (1000 W) F	435.0^e	10	85
	nC_6	$40\ (40)^c$	Xe (300 W) M	434.4	77	76
enzo[b]fluoranthene	nC_8	3.0	Xe (150 W) F	—	77	84
	nC_8	2.5^g	Hg (1000 W) F	397.65	10	85
enzo[j]fluoranthene	nC_8	10^g	Hg (1000 W) F	469.55	10	85
enzo[k]fluoranthene	nC_8	0.1^g	Hg (1000 W) F	403.40	10	85
	nC_8	0.2	Xe (150 W) F	—	77	84
orene	nC_6	$10\ (10)^c$	Xe (300 W) M	317.3	77	76
enzo[a]fluorene	nC_7	$2\ (7)^c$	Xe (300 W) M	346.1	77	76
enzo[b]fluorene	nC_8	$2\ (3)^c$	Xe (300 W) M	338.8	77	76
ole	nC_8	20	Xe (1000 W) F	404.6^f	77	101
ethylcholanthrene	$nC_8:cC_6$	5^d	Hg (125 W) IF	392.5	77	127
	$nC_8:cC_6$	200	Hg (50 W) IF	392.5	77	72
phthacene	nC_9	$7\ (7)^c$	Xe (300 W) M	479.0	77	76
phthalene	nC_5	$40\ (50)^c$	Xe (300 W) M	334.8	77	76
ylene	nC_8	1.0	Xe (1000 W) F	451.1	77	74
	nC_6	2.0^d	L (7 mW) 441 nm	443.95	77	108
	nC_7	$9\ (3)^c$	Xe (300 W) M	443.9	77	76
	nC_6	10^d	Hg (125 W) IF	443.95	77	108
	$nC_8:cC_6$	50^d	Hg (50 W) IF	451.0	77	72
	nC_6	353^d	L (4 mW) 337.1 nm	452.6	77	125
enzo[ghi]perylene	nC_8	0.25^g	Hg (1000 W) F	419.6	10	85
	nC_8	1.0	Xe (1000 W) F	419.5	77	74
	nC_8	3.0	Xe (150 W) F	—	77	84
	nC_8	$7\ (20)^c$	Xe (300 W) M	419.7	77	76

Compound	Matrix^a	ng m$l^{-1\,b}$	Excitation system	Emission wavelength (nm)	Temp. (K)	Ref.
Phenanthrene	nC_6	1.8^d	L (4 mW) 337.1 nm	496.7^f	77	125
	nC_7	10	Xe (1000 W) F	461.6^f	77	74
	nC_6	20 (20)^e	Xe (300 W) M	345.3	77	76
	nC_6:cC_6	100^d	Hg (50 W) IF	345.5	77	72
1-Methylphenanthrene	nC_6	10	Xe (450 W) M	348.0	4.2	90
2-Methylphenanthrene	nC_6	60	Xe (450 W) M	358.5	4.2	90
3-Methylphenanthrene	nC_6	10	Xe (450 W) M	350.0	4.2	90
4-Methylphenanthrene	nC_6	10	Xe (450 W) M	349.5	4.2	90
9-Methylphenanthrene	nC_6	10	Xe (450 W) M	348.5	4.2	90
Pyrene	nC_7	0.7^d	L (4 mW) 337.1 nm	392.0	77	125
	nC_8	3	Xe (150 W) F	—	77	84
	nC_8:cC_6	5^d	Hg (125 W) IF	371.75	77	127
	nC_6	8 (2)^e	Xe (300 W) M	371.3	77	76
	nC_8	10	Xe (1000 W) F	382.4	77	74
	nC_8:cC_6	50^d	Hg (50 W) IF	371.75	77	72
1-Methylpyrene	nC_6	0.2 (0.5)^e	Xe (300 W) M	374.7	77	76
3-Methylpyrene	nC_8:cC_6	200^d	Hg (50 W) IF	375.0	77	72
4,9-Di-*t*-butylpyrene	nC_8:cC_6	200^d	Hg (50 W) IF	375.0	77	72
3,5,8,10-Tetraisopropyl pyrene	nC_8:cC_6	100^d	Hg (50 W) IF	379.25	77	72
Benzo[a]pyrene	nC_8	0.05^g	Hg (1000 W) F	402.95	10	85
	nC_8	0.1^d	Hg (125 W) IF	403.0	77	108
	nC_8	0.1	Xe (1000 W) F	403.0	77	74
	nC_8	0.2	Xe (150 W) F	—	77	84
	nC_8	1 (0.8)^e	Xe (300 W) M	402.7	77	76
	nC_8:cC_6	5^d	Hg (50 W) IF	403.0	77	72
3-Hydroxy-benzo[a] pyrene	nC_8	1	—	422.16	77	101
6-Hydroxy-benzo[a] pyrene	nC_8	10	—	419.38	77	101
Benzo[e]pyrene	nC_8:cC_6	1^d	Hg (125 W) IF	387.75	77	127
	nC_7	10	Xe (1000 W) F	537.0^f	77	74
	nC_8	20 (30)^e	Xe (300 W) M	388.4	77	76
	nC_8	25^g	Hg (1000 W) F	388.20	10	85
	nC_8:cC_6	70^d	Hg (50 W) IF	387.75	77	72
Dibenzo[ae]pyrene	nC_8:cC_6	1^d	Hg (125 W) IF	395.5	77	127
	nC_8:cC_6	80^d	Hg (50 W) IF	395.5	77	72
Dibenzo[al]pyrene	nC_8:cC_6	0.3^d	Hg (125 W) IF	395.25	77	127
	nC_8:cC_6	80^d	Hg (50 W) IF	395.25	77	72

Table 2 (continued)

QUASI-LINEAR LIMITS OF DETECTION, EXCITATION SYSTEMS, TEMPERATURES, AND ANALYTICALLY USEFUL WAVELENGTHS

Compound	Matrix[a]	ng $m\ell^{-1}$[b]	Excitation system	Emission wave-length (nm)	Temp. (K)	Ref.
Dibenzo[ah]pyrene	nC_8	0.1[d]	Hg (125 W) IF	449.15	77	108
	nC_9	0.7[d]	L (7 mW) 441 nm	449.15	77	108
	nC_8:cC_6	40[d]	Hg (50 W) IF	449.25	77	72
Dibenzo[ai]pyrene	nC_8:cC_6	0.3[d]	Hg (125 W) IF	431.5	77	127
	nC_8	1.0	Xe (1000 W) F	431.7	77	74
	nC_8:cC_6	100[d]	Hg (50 W) IF	431.5	77	72
Indeno[1,2,3-cd]pyrene	nC_8	1.0[d]	Xe (150 W) F	—	77	84
	nC_8	1.0[e]	Hg (1000 W) F	462.50	10	85
	nC_8:cC_6	300[d]	Hg (50 W) IF	462.5	77	72
Tryphenylene	nC_7	10	Xe (1000 W) F	461.8[f]	77	74
	nC_8:cC_6	100[d]	Hg (50 W) IF	462.25[f]	77	72

Note: Xe = xenon-arc lamp; L = laser; Hg = mercury lamp; F = broad band filter; IF = interference filter; M = monochromator.

[a] nC_5 = *n*-pentane; nC_6 = *n*-hexane; nC_7 = *n*-heptane; nC_8 = *n*-octane; nC_9 = *n*-nonane; cC_6 = cyclohexane.

[b] The limits of detection in parenthesis refer to limits determined using excitation quasi-lines.

[c] Using signal-to-noise of 3.

[d] Using signal-to-noise of 2.

[e] Broad band emission.

[f] Phosphorescent emission.

[g] Using signal-to-noise of 6.

Partial data reprinted from Lai, E. P., Inman, E. L., Jr., and Wineforder, J. D., *Talanta,* 29, 601, 1982. With permission. Also from Paturel, L., Jarosz, F., Fachinger, C., and Suptil, J., *Anal. Chim. Acta,* 147, 293, 1983. With permission.

strated that the classical problem of the spectral isolation of the quasi-lines of B[a]P and B[k]Ft (which are closely located at 403 nm) could be more easily solved. Figure 8A shows a synthetic mixture of B[a]P, B[k]Ft, and B[ghi]Pe when excited at a nonselective wavelength (385.7 nm) and at selective wavelengths (Figure 8B, C, and D). In Figure 8B the absence of emission of B[k]Ft at 403 nm obviously helps the determination of B[a]P in a mixture.

A comparison between the results obtained with the LESS technique (using a solvent-refined coal sample) and other methods, such as HPLC using fluorimetric detection (NBS data), synchronous fluorescence, room temperature fluorescence, and GC-MS, showed excellent agreement,[77,122] showing the potentiality of the method. It is interesting to emphasize that the determinations which are shown in these papers were carried out without any previous separation, using either standard addition[77,122] or simply the internal reference method.[123]

Interesting results were obtained using LESS[123] when completely deuterated analogs of B[a]P and Pe were employed as internal reference compounds for the direct determination of the nondeuterated correspondent PAH in liquid fuels. Again the results agree quite well with other previous results. The deuterated compounds showed a quasi-linear spectrum, with the emissions blue shifted ca. 55 cm^{-1} (Figure 9), and satisfy the criteria established by the authors such as similar spectroscopic properties, absence in the sample, no direct spectral interference, absence of self-absorption, and the possibility of being excited by the same excitation line as the compound examined.[123] Due to the proximity of the emission lines of the deuterated compound and of the analyte, the authors expect that any quenching ("inner-filter") or enhancement effects will be similar in both compounds.

The utilization of this technique was demonstrated when deuterated (D_{12}) B[a]P was used as an internal reference, B[a]P, B[k]Ft, and B[ghi]Pe being determined by Renkes et al.[124] in extracts obtained from some particulate samples, using diphenylmethane as the extraction solvent. Due to its high boiling point, diphenylmethane provides a high-temperature (240°C) extraction method, which proved to be rapid and efficient. A NBS certified standard — urban dust — sample was examined and good agreement was found between the results, although a slight deviation to the high side was observed.

Experiments using a pulsed nitrogen laser (337.1 nm, 4 mW) were also carried out by Vershinin and co-workers.[125] For such experiments P, Ch, and Pe were dissolved in *n*-hexane and frozen to 77 K. It is interesting to observe that the radiation from the laser was introduced through the frozen matrix into the microcell, from top to bottom, the luminescent signal being observed from the side of the cell. According to the authors, the quasi-lines wavelengths agreed with the previous published results (with an uncertainty of 0.1 to 0.2 nm); also, the number of lines observed were the same as in classical broad lamp excited spectra. Comparison of the spectra obtained with laser excitation and the spectra obtained with an instrumental set-up which employs mercury lamp excitation and a two monochromator excitation and emission spectrofluorimeter (a commercial instrument) showed that less resolved spectra were, however, observed with the commercial instrument. High scattering was observed with the laser system, which limited the detection limit. The coincidence of the quasi-lines, with previously published spectra, even in complex mixtures, made possible the identification of several PAHs, particularly if the relative intensities were taken into consideration. A practical application of the technique was carried out by the qualitative examination of a sample of heat-transfer oil, dissolved in *n*-hexane, when it was possible to identify P, 1-Me-P, 3-Me-P, 4-Me-P, and B[e]P from the fluorescent or phosphorescent quasi-lines present.[125]

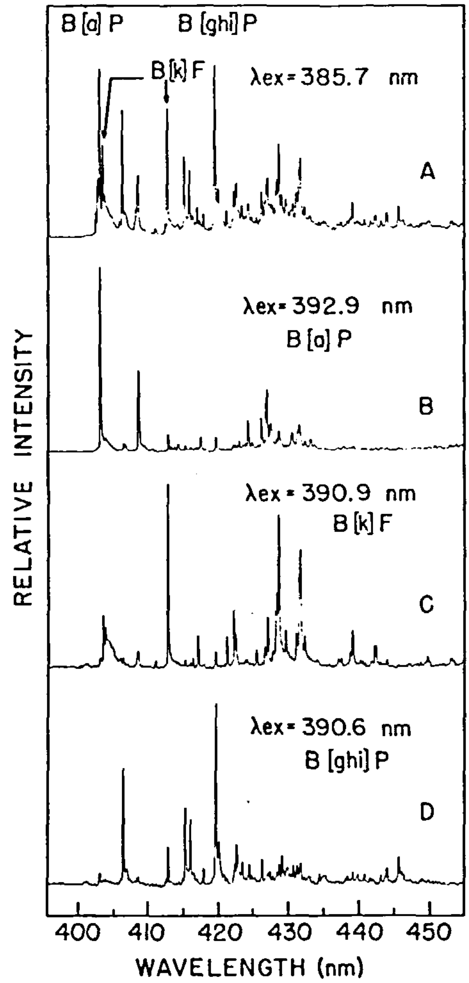

FIGURE 8. Laser selectively excited quasi-linear fluorescence spectra of a synthetic mixture in *n*-octane at 15 K of benzo[a]pyrene, benzo[k]fluoranthene, and benzo[ghi]perylene. (Reprinted with permission from Yang, Y., D'Silva, A. P., and Fassel, V. A., *Anal. Chem.*, 53, 894, 1981. Copyright 1981 American Chemical Society.)

Limits of detection were obtained (considering a signal-to-noise ratio of two) and are shown in Table 2. The percent of RSD was 5%, much higher if compared with room-temperature measurements (0.6%). This was attributed to the differences in freezing rates. The presence of A in the signal intensity of Ph (even at a ratio of 80:1) did not affect the intensity; however, Ch was affected (at a ratio of >2:1) as the Ch quasi-line located at 379.9 nm is affected by the A emission at 381.3 nm.[125]

2. *Selection of Wavelength of Excitation*

a. *Filters*

Optical filters were, in the beginning, most commonly used for selection of the wavelength of the radiation used for excitation. Soviet workers have used filters of the UFS type. The UFS-3[40,44,54] is the most frequently used and behaves like Wood's glass, isolating the 320- to 390-nm region. Eichhoff and Köhler[52] employed a combination of

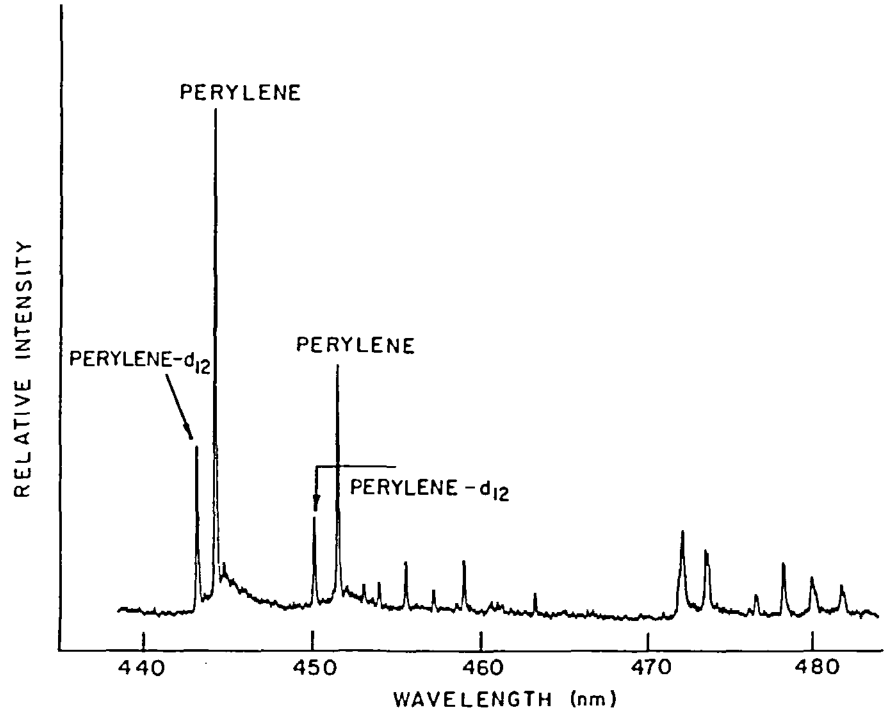

FIGURE 9. Laser selectively excited quasi-linear fluorescence spectrum of perylene in crude oil sample using perylene-d_{12} as internal reference. (Reprinted with permission from Yang, Y., D'Silva, A. P., and Fassel, V. A., *Anal. Chem.*, 53, 2107, 1981. Copyright 1981 American Chemical Society.)

two glass filters. Interference filters were also employed in a series of works;[10,71,73,92,96] these filters have narrow bandwidths — 14 nm at 250, 30 nm at 300 nm. Santoni and Mandon[84] recently employed a wide band filter (270 to 360 nm) for the simultaneous excitation of six PAHs. A cut-off filter was used by Colmsjö and co-workers,[75,78,80,82] which absorbs the radiation with $\lambda > 348$ nm.

b. Monochromators

The use of a monochromator to select the excitation wavelength radiation has been increasing, especially in the last 5 years.[14-63,81,88,91,93-98] Lavalette and co-workers[44] and Fedoseeva and Khesina[63] pioneered this approach (frequently utilized in low-resolution spectrofluorimetry) which has been called later HRS.[88-91]

Fedoseeva and Khesina[63] used, as an excitation monochromator, a double-pass prism monochromator of Soviet construction (ZMR-3). Lavalette et al.[44] employed a dual quartz prism monochromator for excitation similar to that employed for recording the emission spectra. Medium-resolution monochromators have been used in such excitation assemblies which can isolate a spectral band-pass with a full width at half-maximum (fwhm) of 2.5 to 4.0 nm.[88-91,93-98]

3. Sample Handling System

The sample handling system employed to work with quasi-linear spectra can be divided into (1) the types used for analytical purposes using glass or quartz tubes where liquid nitrogen is the usual liquid coolant (owing to its low cost and wide availability) and (2) the types used in fundamental studies and in recent analytical studies, cryostats or closed-cycle cryogenerators, where the coolant can be either liquid or solid nitrogen, or even liquid helium.

From the earlier period until ca. 1976, for analytical applications, the usual arrangement was a Dewar flask where a sample tube is introduced directly in the liquid nitrogen. A quartz[63] or, more frequently, an ordinary glass test tube[48,49,54,60,72] was used to hold the sample. Dikun[48] used two concentric test tubes, the samples being frozen between the wall of the two tubes, to study the effect on the signal of the thickness of the sample layer; the only effect observed was the loss in intensity when this thin arrangement was used, in comparison with the use of a test tube of 12 to 14 mm in diameter.

The inner diameter of the sample tube (used with the Dewar flask) was usually in the range of 7 to 15 mm, and the capacity ranges from 1 to 10 m*l*. The Dewar is in most cases constructed of glass. Jäger and Lugrová[55] employed a specially made type of glass cell with a disc-shaped foot to ensure its attachment to the bottom of the Dewar. Eichhoff and Köhler[52] used a horizontal sample holder on top of a copper cold-finger similar to the sample device used by Bowen and Brocklehurst;[28,29] Eichhoff and Köhler[52] used the smallest possible volume of sample (0.06 m*l*) to solve a problem of freezing rate reproducibility; with the increase of the volume, a loss in resolution was observed by these workers.

Muel and Lacroix[47] used two types of sample cells, a glass tube and a copper tube, but no more details were given in the published article.

Causey et al.[108] proposed a new laboratory-constructed sample cell and cryostat that used as a coolant liquid nitrogen. This set-up is similar to those suggested by Parker[126] and Svishchyov,[111] however, without the disadvantage of the previous design[111] which requires warming the whole cryostat when it is necessary to change a sample. Also, the system proposed provides for the possibility of freezing the sample cell in liquid nitrogen and later attaching it to the copper cryostat. This new design was compared with the classical commercial quartz tube and Dewar flask and it was found that in the former, the frozen sample was at 80 K and the mean cooling rate was 75 K min^{-1} vs. 77 K and 540 to 720 K min^{-1} in the latter. Precision was however much better with the new proposal; using Co for instance, with concentrations of 2.5 10^{-5} and 2.5 10^{-7} *M* the RSDs decreased from 9.7 and 12% to 1.5 and 2.5%. In a further work this cell-cryostat set-up was used in the determination of PAHs in coal-tar pitch extracts.[86]

The freezing rate effect in the intensity ratio of a Co doublet (445.15 and 443.33 nm) was also compared using both systems and a relatively small increase was observed — when the copper cell-cryostat was examined — confirming the previous observations of Personov, that slow freezing affects the Co doublet.[49]

Colmsjö and co-workers[75,78,80-82,103] used a laboratory-built sample cell for the study and application of quasi-linear spectra for the detection and determination of several PAHs. The cell was later modified to work at 63 K by evacuation of liquid nitrogen using a vacuum pump and thus produced solid nitrogen. The volume used in this cell was indeed small (50 μl) and the time required to freeze the sample was very fast (<1 sec). The further decrease of the temperature resulted in a better resolution of the peaks, which improved the qualitative characteristic of the Shpol'skii method, and consequently the possibility of identifying PAHs present in a mixture.

Closed-cycle helium cryogenerators using copper sample cells or small diameter silica tubes (even five tubes) and temperatures which range from 16 to 10 K have been proposed in recent papers.[77,85,86,88-91] To avoid the effect of freezing rate, the cell compartment is usually previously frozen in liquid nitrogen. One of the devices was that described in a work by Paturel et al.,[85] where the Shpol'skii spectra can be examined at 10 K. The sample cell system comprised a closed-cycle cryogenerator where a three-compartment cell was assembled. A fast heat exchanger permits a fast cooling and heating process. Although 1 hr is necessary to cool the sample from ambient temperature to 10 K, the three-compartment cell system provides the possibility of analyzing three samples, in sequence, and, according to the authors, with good reproducibility.[85] Very narrow and intense emissions were observed using this temperature (Figure 10).

The temperature of 4.2 K, using a helium cryostat, has also been used[88,91,94,95] and, as expected, an extraordinary improvement in the resolution was observed compared with the resolution observed at 77 K (Figure 5). However, when a closed-cycle cryogenerator assembly (15 K) and helium cryostat (4.2 K) were compared, the resolution improvement was of a small extent, affecting mainly the phonon wing and the background signal.[88] The authors concluded that closed-cycle cryogenerators could substitute (with an advantage) the helium cryostat as there is no necessity of a helium supply.[88]

4. *Emission Monochromators*

One of the necessary conditions for the successful observation of the Shpol'skii effect is the use of a monochromator of moderate to high resolution, one which is able to isolate a spectral bandpass of 0.2 nm or less (typically using monochromators of reciprocal dispersion in the range of 2.0 to 0.5 nm mm^{-1}). To be analytically useful the instrument must also have high light throughput. Obviously, when spectra are recorded with an instrument of low resolving power, little difference in the width of the lines is observed in glassy and Shpol'skii polycrystalline matrices and loss of the fine structure is observed. This results from the fact that with a low-resolution monochromator the bandwidths observed are merely images of the spectrometer entrance slit. Also, if the sample has a high-intensity broad background luminescence spectrum, using the low-resolution spectrofluorimeter makes it impossible to detect low concentrations of PAHs even in Shpol'skii conditions. An example of such a problem can be seen in Figure 11. In Figure 11A the fluorescence spectrum of a sample of used lubricant oil (dissolved in *n*-octane and frozen at 77 K) is shown using a double monochromator, low-resolution spectrofluorimeter, and in Figure 11B, the same sample was obtained using a high-resolution monochromator assembly where it was possible to observe the quasi-linear emission of B[a]P. Although several attempts were made with different excitation wavelengths and slits with the low-resolution instrument, only broad emissions were observed.[127]

The first observation of the phenomenon by Shpol'skii et al.[1] was made using a glass prism spectrograph with a reciprocal dispersion of 2.5 nm mm^{-1} in the region of 400 nm.

Bowen and Brocklehurst[28,29] observed the effect with a Hilger constant deviation spectrometer with a glass prism. In the blue region, the wavelength accuracy was of ±0.1 nm or better and in the yellow region of ±0.5 nm.

Spectrographs were frequently used by Soviet workers. In his first review concerning the phenomenon in 1959, Shpol'skii[7] refers to two spectrographs. One had a glass prism, with a reciprocal dispersion of 2.7 nm mm^{-1} at 400 nm, and the other had a plane diffraction grating which produced a reciprocal linear dispersion of 0.49 nm mm^{-1}. Similar instrumentation was used by Il'ina and Personov for qualitative analysis work.[46]

Muel and Lacroix[47] and Lavalette et al.[44] employed one monochromator with two flint prisms. This had "great luminosity and purity of isolated light". Shpol'skii and Personov[51] referred, in 1962, to the use of a spectrograph with a reciprocal dispersion of 0.3 nm mm^{-1} in a review concerning the application of the method to analytical purposes. Jäger and Lugrová[55,56] have been applying the effect to analysis using glass prism spectrographs (KSA-1) with a dispersion of 0.55 nm mm^{-1} at 400.0 nm. Most Soviet workers use the ISP-51, a spectrograph. This has three glass prisms and pro-

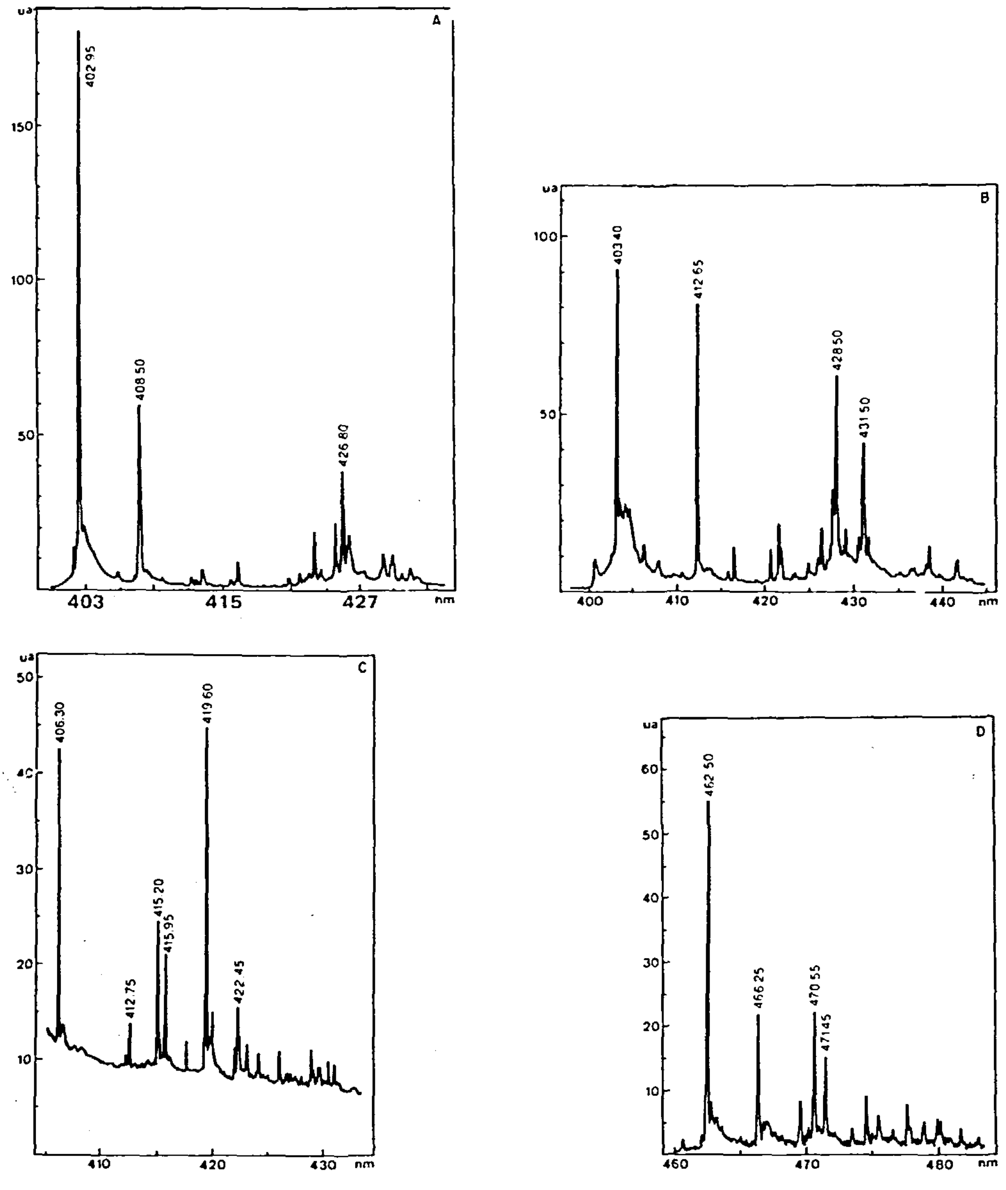

FIGURE 10. Broad-band filter-excited (1000-W mercury lamp) fluorescent quasi-linear spectra of some PAHs; (A) benzo[a]pyrene; (B) benzo[k]fluoranthene; (C) benzo[ghi]perylene; and (D) indeno[1,2,3-cd]pyrene, in *n*-octane matrix at 10 K. (From Paturel, L., Jarosz, F., Fachinger, C., and Suptil, J., *Anal. Chim. Acta*, 147, 293, 1983. With permission.)

duces a dispersion of 0.65 nm mm^{-1} at 400.0 nm.[36,39,45,48,49,62,64,90] Also, the use of a diffraction monochromator — DFS 12 — is frequently reported,[61,66,79,100] which is a double-grating, Czerny-Turner assembly, with a reciprocal linear dispersion of 0.5 nm mm^{-1}.[107] A high-transmission spectrograph has also been used[40,64] (ISP-73); this is a dual glass prism spectrograph with a reciprocal dispersion of 2.0 nm mm^{-1} at 410 nm and a relative aperture of 1:4. Eichhoff and Köhler[52] used a spectrograph with three glass prisms; no other details were given, however.

In recent papers, spectrometers using monochromators (using Littrow, Ebert, or Czerny-Turner mounting) with reciprocal dispersion in the range of 1.60 to 0.5 nm mm^{-1} have been employed in the instrumental assemblies.[71,72,75,79,81,100,108]

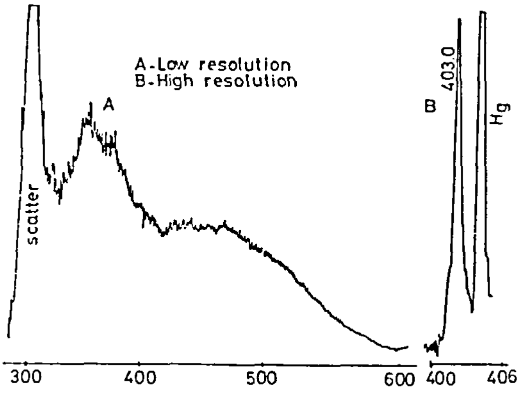

FIGURE 11. Low-resolution (A) and high-resolution (B) spectra of a used lubricant oil sample diluted in *n*-octane and frozen at 77 K, showing in the latter case a 403.0-nm quasi-line, attributed to B[a]P.

5. Detection of Luminescence Radiation

Most of the earlier studies of quasi-linear luminescence spectrometry were conducted with the photographic plate system of detection, or spectrographs using photoelectric attachment. However, at present, photomultipliers are the detectors in general use. A FEU-17 photomultiplier was used in the past in some of the Soviet work.[53,54] This photomultiplier has a photocathode of antimony-cesium, but no other specification was revealed from the published papers. In recent papers, this detector has been replaced by the FEU-17A, which has a spectral response in the range of 300 to 600 nm.[107] Muel and Lacroix[47] and Lavalette et al.[44] used the photometric technique with an EMI 6685 B photomultiplier as the detector; this photomultiplier was superseded later by the EMI 9502B, which has an S-11 response.

Eichhoff and Köhler[52] used a spectrograph fitted with an RCA 1P 21 photomultiplier (S-4 spectral response) to provide a direct reading photometric system. In a preliminary work evaluating the potentiality of quasi-linear luminescence, Kirkbright and de Lima[71,72] used an end-window photomultiplier (EMI 9601B) which has an S-11 spectral response. Later in the continuation of this work,[73,108] an EMI 6256 S was used — an S-13 spectral response photomultiplier having however a specially processed cathode, with a low dark current. When this detector was used in conjunction with photon counting[108] a further reduction of ca. 90% was observed in the dark current when the temperature was decreased from room temperature to dry-ice temperature. Other photomultipliers, such as the Hamamatsu R-106 (S-19) and R-955 (S-20), the EMI 9789QB (a bialcaly-type response), and the classic RCA 1P 28 (S-5), have been used by other workers. An advance in the detector area (and signal processing) was that utilized by Fassel and co-workers,[123] which uses a diode array detector in quasi-linear luminescence.

6. Signal Processing

Although in general the signal originated from the detector is simply amplified and then fed to a chart recorder, in the literature reviewed there are some cases where some other forms of signal processing have been used associated with the analytical application of the Shpol'skii effect.[77,85,108,121-124]

DC integration, photon counting, and signal averaging (using a refractor plate scanning system) were examined by Causey et al.[108] In the case of integration, both constant time and constant charge were tested and improvements in the RSD (with B[a]P in *n*-

octane) were observed, from 25% (using analog direct read-out) to 3 or 1.4%, respectively.

With the optical assembly employed a limit of detection for B[a]P (direct read-out) was 126 ng ml^{-1}. With the integration systems (using the same optical set-up) a decrease of ca. 2.5 decades was found. Although such improvement was found, the integration system lacks the possibility of a qualitative identification and consequently does not exclude the parallel use of a recorder for the scanning of a chosen wavelength range, when necessary.[108]

The technique of photon counting, which has been widely employed in molecular spectrofluorimetry (after being examined by the same authors), revealed no improvements in the limit of detection as a result of the presence of a large background (mainly due to scattered light from the polycrystalline matrix). Longer counting times (15 to 60 sec) can improve this situation, but this seems to be, according to the authors, unsatisfactory from the point of view of routine analysis.[108] Despite this, the photon counting method, followed by a digital-analog conversion and recorder tracing, was successfully employed by Wehry and co-workers[128] in matrix isolation experiments.

Signal averaging using repetitive optical scanning, when applied to Shpol'skii conditions, showed to be a promising technique.[108] Although the oscillating refractor plate used only allows the possibility of examining a spectral range of 2 to 3 nm, the technique was suggested for the detection of small amounts of PAHs and for fundamental studies in relation to the effect of parameters such as cooling rate, concentration, or matrix in the quasi-linear bandwidth and intensity, principally if lower temperatures and small spectral bandwidths are employed.[108]

Time-resolved spectra have also been employed using a laboratory-constructed gated integrator[77] or a commercial boxcar averager.[121-123] Synchronous detection (lock-in) has been used by Pasturel et al.;[85] it seems that in the instrumental assembly proposed, the excitation signal is modulated using a mechanical chopper.

A recent and interesting approach was that using an optical multichannel analyzer which employs a diode array detector.[123] With this signal processing system, a 10-nm spectrum range can be integrated and run in 10 sec. Also the instrumental assembly provides for the possibility of using either the diode array detector or a photomultiplier.[124]

D. Matrix Isolation in Shpol'skii Matrices

Another sampling method which, however, differs completely from the frozen solution Shpol'skii technique — and is in reality an independent method — is that employed in the matrix isolation (MI) technique. Usually, in this technique, the sample (liquid or solid) is vaporized, diluted with a large excess of an inert gas (argon, nitrogen, or xenon) with a sample to gas ratio of 1.10^5 to 1.10^7, and deposited on a cold surface (15 K) such as an sapphire window or a gold-plated copper surface. The analytical application of MI has been extensively examined and reviewed by Wehry and Mamantov.[129,130] The reading of these reviews is worthwhile for any analyst involved with the utilization of the Shpol'skii effect for PAH analysis, as the advantages and disadvantages of both methods are widely discussed. By using an inert gas, larger dynamic ranges in the calibration curves (such as five decades) were observed in comparison with frozen-solution Shpol'skii technique.[128] When the deposition is carried out in the presence of Shpol'skii matrix, annealed at 150 or 155 K and finally cool-down to 15 K, a much finer (quasi-linear) spectrum is observed.[131,132] The effect of changing the matrix from N_2 to *n*-heptane can be seen in Figure 12.[132]

With this modification it was possible to observe quasi-linear spectra of several four- and five-ring PAHs (exceptions were tetracene and pentacene) using *n*-heptane. Also the method opens up the possibility of observing quasi-linear luminescence independ-

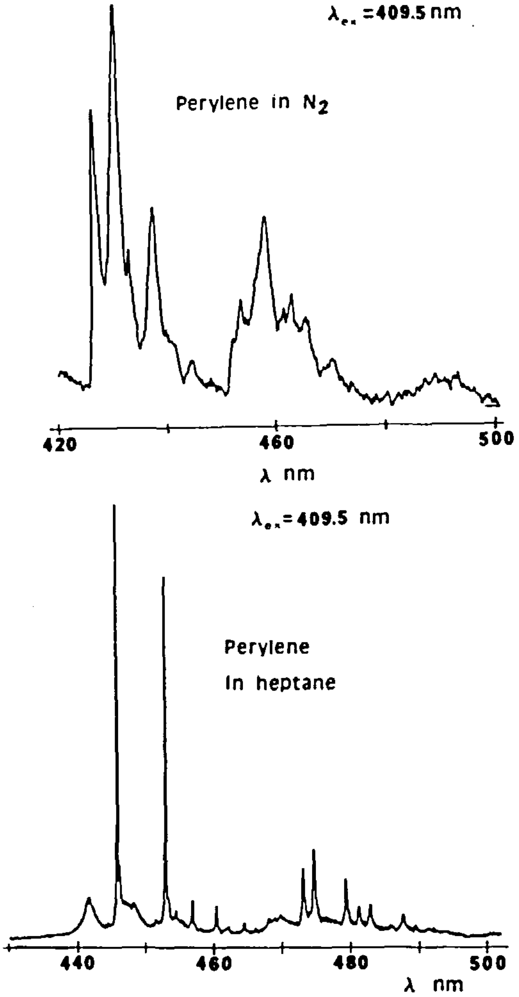

FIGURE 12. Matrix isolation fluorescent spectra using dye laser excitation of perylene in a nitrogen matrix and in an *n*-heptane annealed matrix. (Reprinted with permission from Maple, J. R., Wehry, E. L., and Mamantov, G., *Anal. Chem.*, 52, 920, 1980. Copyright 1980 American Chemical Society.)

ent of the matrix compatibility or even the analyte solubility in the matrix. Although the analyte must be volatile and a longer time is involved in the preparation of the sample in the MI method, there is a possibility of examining solid samples[133] without the necessity of previous extraction. High-intensity excitation sources (2.5-kW mercury-xenon arc lamp)[132,133] and tunable dye lasers have been utilized and good results have been found. Comparison of the results using a NBS certified shale oil sample shows very close results (certified 21 ± 6 and found 23 ± 4 $\mu g\ g^{-1}$).[133] Laser-induced MI spectrofluorimetry using Shpol'skii matrices have been recently applied in analytical studies with some alkylated and methoxilated derivatives of B[a]P.[130] Polar aromatic compounds were also studied in argon or fluorocarbon matrix using site-selection fluorimetry.[135]

E. Limits of Detection

Table 2 shows some quasi-linear limits of detection collected from various sources of the literature examined with the respective excitation system and temperature utilized. Although a real comparison between the limits of detection presented on Table 2 is difficult as different instrumental set-ups have been employed and different experimental and mathematical approaches have been used for their determination, it is clearly seen in some cases that, as expected, the limit of detection decreases when a powerful excitation source or lower temperatures are used.

Winefordner and co-workers[76] observed that much better limits of detection were found, however, by using room temperature fluorescence (RTF), which were three or four decades smaller. This has been explained as a result of several factors which are present in RTF, such as lack of scatter, large excited sample volume, and espectral bandwidth and depth of excitation, which in quasi-linear luminescence are the opposite.[76] Despite that, the optimum quasi-linear limits of detection quoted in Table 2 are, however, lower when compared with data obtained at low temperature (77 K) using *n*-heptane as matrix and low-resolution spectrofluorimetry.[136]

F. Quasi-Line Atlas and Computer-Assisted Spectrometry

After examining 105 polycyclic aromatic organic compounds Colmsjö and Östman published these spectra in an extremely useful quasi-line atlas,[106] using a temperature of 63 K and, most of the time, *n*-hexane as a matrix. Of the compounds examined, 14 (such as dibenzothiophene, phenoxazine, pentacene, thioanthrene, benzo[c]phenanthrene, etc.) showed either a weak or absent luminescent signal. In some cases, although nonquasi-linear luminescence was present, the spectrum was presented for comparison. Besides others, these being an interesting series of compounds, were several anthracenes substituted at the position 9; with the exception of the 9-phenylanthracene, all the other compounds (including 9-methyl-, 9-cyano-, 9-bromo-, 9-chloro-, and 9-methoxy-) showed quasi-linear emission in *n*-hexane. Also, in contrast with 9-methyl-anthracene, the 2-methyl derivative showed a broad spectrum, demonstrating the importance in the choice of an appropriate matrix to observe the phenomenon.

Of the four amino compounds examined most showed a broad emission associated with quasi-lines emissions; the unique exception was 1-aminopyrene, which showed a perfect quasi-linear spectrum.

The relation between quasi-linear spectrum aspect and the position of a substitution (in position 1) of several pyrene derivatives (such as 1-cyano-, 1-methoxy-, 1-chloro-, 1-bromo-, 1-amino-, 1-hydroxy-, 1-phenyl-) was discussed in a later paper.[137]

Two computer file-search and identification programs similar to other systems previously used in infrared, nuclear magnetic resonance, UV, or MS, and recently in the structural intepretation based on the fluorescence spectra[138] were proposed by Soviet authors[139,140] based on several Shpol'skii effect spectra, taken from another atlas quoted in References 139 and 140 and produced by Teplitskaya et al. (published by the Moscow State University in 1978). Vershinin et al.,[139] using this atlas, chose the quasi-linear luminescence spectra (in the 360- to 600-nm region) of 85 PAHs (in *n*-hexane and at 77 K) which were introduced into a computer, with a file-search and identification program relating the compound's wavelength (in Å) and its respective name. Although the relative intensities were not taken into consideration, the program established could be used for the identification of most of the compounds in the data base. The authors[139] also proposed a characteristic number, based on the number of quasi-lines and the possibility of spectral overlap, called "specificity", which is in fact an identification factor.

Diphenyl, fluorene, P, and B[a]P, despite having "medium specificity", can be identified in mixture through this program without resorting to selective excitaton, previous chromatographic separation, and lower temperature measurements.[139]

The other file-search system, basically similar to the previous one, was that proposed concomitantly by Pugovkin et al.,[140] which employs the same data from the Teplitskaya and co-workers' atlas. All of the 100 spectra of the atlas were introduced into the computer library and a probability identification criterion called IDEN was employed. The spectra of several samples, either single compounds or complex mixtures, after being examined by this system, resulted in the identification of the most probable compound(s).

It is certainly expected that this approach will be used more and more in the near future, especially in the centers where it is necessary to have a quick and reliable way of identification, and even determination of PAHs as presently done with MS or a hyphenated technique such as GC-MS. The specific nature of quasi-linear spectra suggests also that in the commercial instruments — which are available for the utilization of the effect in analysis[130] — a spectra library and searching computer program coupled to the instrument will be of great value.

III. CONCLUSION

Due to its extraordinary "fingerprinting" capability the technique which uses the Shpol'skii effect for the detection of trace amounts of PAHs (even making possible the differentiation of very similar isomers)[36] and some heteroanalog compounds is an analytical method which deserves the attention of any worker or group challenged with such a problem. The examples in the literature of the possibilities which the Shpol'skii method offers for the identification of similar isomers are numerous; one of the recent cases is that described by Garrigues and Ewald[96] when some methylchrysenes were identified in crude oil samples. Also, in the few cases where quasi-linear spectroscopy was compared with MS (or capillary-column gas chromatography-MS) this method proved to be superior in the unambiguous identification of some alkylated derivatives of B[a]A[77] or P.[82] The importance of quasi-linear luminescence in the trace detection of some PAHs is without question because of the well-known carcinogenic character of some members of the family; the carcinogenic action sometimes appears or drastically increases simply by changing, for instance, the position of a methyl substituent in a PAH nucleus.[96] This frozen solution method is simple and well established, and the widespread utilization cannot be hindered as it was in the past, because of the lack of appropriate instrumentation as, according to Wehry and Mamantov,[130] there are instruments commercially available which can be used. Also, this problem can be solved very simply, as we can deduce from the previous review, using modules such as a power supply and excitation source, monochromators, a sample handling device, etc., and assemblying them together.

A possible restriction is due to the fact that the technique is limited to the analysis of fluorescent or phosphorescent, unpolar or weakly polar compounds which could be solubilized in *n*-paraffins and a few other Shpol'skii solvents,[73] although, until 1974, nearly 500 compounds presented quasi-linear spectra[26] when the fundamental work was carried out. It is, however, true that only time will provide the answer related to what percent of those compounds have the urgent need of being determined at the trace level.

From the point of view of quantitative analysis, although the Shpol'skii effect has been largely used for the determination of PAHs, as we can see in this review, there are some critical parameters such as the freezing rate,[16-20] analyte concentration,[21-23] final temperature,[17,78] and the necessity of working with an appropriate Shpol'skii solvent[9,10,28,29,75,78] which affect the signal intensity (and bandwidth) and consequently, the analytical results. Other points which have been pointed out as problems are the limited linear dynamic ranges of the calibration curves[130] and the strong scatter observed.[118]

These problems were extensively examined by Fassel and co-workers[77] and it was found that most of them, such as signal irreproducibility, can be solved by using a careful and reproducible freezing rate and low analyte concentration (ca. $\leqslant 1.10^{-6}$ *M*). Also, the scatter can be reduced if the excitation is >10 nm distant from the emission; the matrix compatibility does not seem to be a serious problem, as *n*-heptane can be utilized with several PAHs with three- to six-ring structures.[77] Although most of the published linear dynamic ranges presented 2 to 2.5 decades, Fassel and co-workers[77] found ranges above 3.5 decades. To compensate for "inner-filter" or enhancement effects, the same authors utilized the standard addition and internal standard method.

The internal standard or the standard addition method alone (or associated to the internal standard method) continues being used to solve the problems of irreproducibility of the signal due to formation of analyte aggregates during the freezing process (microcrystalline aggregates or preaggregates), cell position, and excitation source fluctuation. According to Yang et al.,[121,123] although the standard addition method has the advantage of considering any "inner-filter" or signal enhancement effect, it has however the disadvantage of being time consuming. In this last aspect the internal standard method is much simpler. Sometimes, the addition of a compound to be used as the internal standard has been substituted by the reading of a quasi-linear signal of another compound already present in the sample. The choice of an internal standard compound must, however, be made with care; along with the expected spectral characteristics, the compound chosen must behave similarly to the analyte from the point of view of the freezing characteristic and present none or minimum perturbation in the analyte signal.[90,91] A clever approach in relation to the use of the internal standard was that proposed by Yang et al.[123] when, as the internal standard for the determination of B[a]P and Pe, the respective deuterated analogs of these compounds were employed. Very recently another method of standardization came to our attention; this method uses as a standard a scattered line (from a mercury lamp used for excitation) with success.[141]

The determination of the accuracy of the results is still being examined. For instance, the quantitation of individual components of synthetic mixtures of monomethylphenanthrene isomers was found by Rima et al.[90] to be 15 to 24% higher in relation to the real ones. These authors, however, concluded that these results could still be considered as satisfactory, due to the low concentrations involved (2 to 3.10^{-7} *M*) and to the similarity of the molecular structure of the analytes. As previously reported, favorable results were also found by Yang et al.,[123] when a solvent-refined coal liquid was analyzed (using selective laser-excited technique) and the results were compared with results found by other techniques. Positive errors in the range of 1 to 16% were found in this case.

Finally, we can conclude from the present review that due to its simplicity in operation low-temperature luminescence spectroscopy using the Shpol'skii method will continue to attract the attention of analysts interested either in further improvements in the method or in its application for the determination of PAHs and related compounds in "real" samples. The use of very low temperatures (lower than 77 K) where much better spectra resolution is obtained, associated with selective excitation, seems to be the most desirable way of utilizing the full potential of the effect as an analytical tool. Despite the cost involved when a tunable dye laser excitation system is employed, progress has been made in recent years.[141] We expect that as a result of the recent trend towards low-cost tunable dye lasers[142] its utilization as an excitation source in quasi-linear luminescence will grow even more.

The painstaking work carried out and the great efforts made in the past, which will certainly continue in other directions such as the matrix isolation technique,[128-135] site selection,[117,120] and supersonic jet (or rotationally cooled) spectroscopy,[143] will decide the exact role of the Shpol'skii luminescence method among those other modern low-temperature luminescence methods and the other methods principally utilized for the determination of trace quantities of PAHs and related compounds.

ACKNOWLEDGMENTS

I would like to thank Ms. M. J. M. Gradim for the library reference scan, Ms. S. G. de Lima for the linguistic advice, and my wife for her continuous help throughout the writing of this review.

REFERENCES

1. Shpol'skii, E. V., Il'ina, A. A., and Klimova, L. A., Fluorescence spectrum of coronene in frozen solutions, *Dokl. Akad. Nauk SSSR*, 87, 935, 1952 (Engl. transl., Nat. Res. Council, Canada, TT-467).
2. Ginzburg, V. L., Kadomtsev, B. B., Kapitza, P. L., Neporent, B. S., Personov, R. I., and Rozenberg, G. V., Éduard Vladimirovich Shpol'skii (on his eightieth birthday), *Sov. Phys. Usp.*, 15, 667, 1973.
3. Blokhintsev, D. I., Bolotnikova, T. N., Ginzburg, V. L., Zel'dovich, Ya. B., Kadomtsev, B. B., Kapitza, P. L., Malov, N. N., Rozenberg, G. V., Semenov, N. N., Suvorov, S. G., Ugarov, V. A., and Khoklov, R. V., Éduard Vladmirovich Shpol'skii (obituary), *Sov. Phys. Usp.*, 19, 102, 1976.
4. Feofilov, P. P., S. I. Vavilov, the founder of the Soviet school of luminescence, *Sov. Phys. Usp.*, 4, 770, 1962.
5. Shpol'skii, E. V., *Atomic Physics*, Ilife, London, 1969.
6. Hindmarsh, W. R., Physics explained, *Nature (London)*, 224, 1135, 1969.
7. Shpol'skii, E. V., Emission spectroscopic analysis of organic compounds, *Sov. Phys. Usp.*, 2, 378, 1959.
8. Shpol'skii, E. V., Line fluorescence spectra of organic compounds and their applications, *Sov. Phys. Usp.*, 3, 372, 1960.
9. Shpol'skii, E. V., Problems of the origin and structure of the quasilinear spectra of organic compounds at low temperatures, *Sov. Phys. Usp.*, 5, 522, 1962.
10. Shpol'skii, E. V., New data on the nature of the quasilinear spectra of organic compounds, *Sov. Phys. Usp.*, 6, 411, 1963.
11. Klimova, L. A., Nersesova, G. N., Naumova, T. M., Oglobina, A. I., and Glyadkovskii, V. I., Investigation of the nature of the luminescence centers in frozen paraffin solutions, (transl.), *Bull. Acad. Sci. USSR, Phys. Ser.*, 32, 1361, 1968.
12. Pfister, C., Solid solutions of aromatics in n-paraffins (Schpolskii effect). I. Isolated molecules in fast frozen samples, *Chem. Phys.*, 2, 171, 1973.
13. Pfister, C., Solid solutions of aromatics in n-paraffins (Schpolskii effect). II. Aggregates or crystallites in annealed samples, *Chem. Phys.*, 2, 181, 1973.
14. Lamotte, M. and Joussot-Dubien, J., Dispersion states and orientation of aromatic solutes in monocrystalline matrices of n-heptane, *J. Chem. Phys.*, 61, 1892, 1974.
15. Merle, A. M., Lamotte, M., Risemberg, S., Hauw, C., Gaultier, J., and Grivet, J. Ph., Study of the multiplet nature in Shpol'skii effect: host n-heptane crystalline structure by X-ray diffraction and guest coronene position by ESR, *Chem. Phys.*, 22, 207, 1977.
16. Dekkers, J. J., Hoornweg, G. Ph., Visser, G., Maclean C., and Velthorst, N. H., Some characteristic features of Shpolskii spectra. The key and hole rule for Shpol'skii systems, *Chem. Phys. Lett.*, 47, 367, 1977.
17. Dokunikhin, N. S., Kizel, V. A., Sapozhnikov, M. N., and Solodar, S. L., The relationship between quasi-linear spectra and the process of crystallization, (transl.), *Opt. Spectrosc. (USSR)*, 25, 42, 1968.
18. Grebenshchikov, D. M., Kovizhnykh, N. A., and Kozlov, S. A., Effect of polymorphism of N-paraffin crystals on the luminescence of additive coronene molecules, (transl.), *Opt. Spectrosc. (USSR)*, 37, 155, 1974.

19. Gurov, F. I. and Nersesova, G. N., Effect of crystallization conditions on the fluorescence spectra of frozen n-paraffin solutions, (transl.), *Bull. Acad. Sci. USSR, Phys. Ser.*, 34, 1135, 1970.
20. Gurov, F. I., Spectral luminescence analysis by Shpol'skii method, (transl.), *J. Appl. Spectrosc. (USSR)*, 18, 113, 1973.
21. Shpol'skii, E. V., Klimova, L. A., Nersesova, G. N., and Glyadkovskii, V. I., Concentration dependence of the fluorescence and the absorption spectra of frozen paraffin solutions of naphthalene, (transl.), *Opt. Spectrosc. (USSR)*, 24, 25, 1968.
22. Klimova, L. A., Oglobina, A. I., and Shpol'skii, E. V., On the concentration dependence of the sharpness of the spectra of aromatic hydrocarbons in frozen n-paraffin solutions, (transl.), *Bull. Acad. Sci. USSR, Phys. Ser.*, 34, 1210, 1970.
23. Ruziewicz, Z., Quasilinear luminescence and absorption spectra of polyatomic organic molecules, *Postepy Fiz.*, 24, 311, 1973 (British Library transl. RTS 9052).
24. Personov, R. I., Solodunov, V. V., Korotaev, O. N., and Godyaev, E. D., Nature of the narrow lines and multiplets in the sharp-line spectra of complex organic compounds, (transl.), *Bull. Acad. Sci. USSR, Phys. Ser.*, 34, 1131, 1970.
25. Rebane, K. K. and Khizhnyakov, V. V., Theory of quasi-line electronic-vibrational spectra in crystals. II. Comparison of the Shpol'skii effect with the Mössbauer effect, (transl.), *Opt. Spectrosc.*, 14, 262, 1963.
26. Shpol'skii, E. V. and Bolotnikova, T. N., Modern trends in quasi-linear spectra studies, *Pure Appl. Chem.*, 37, 183, 1974.
27. Richards, J. L. and Rice, S. A., Study of impurity-host coupling in Shpolskii matrices, *J. Chem. Phys.*, 54, 2014, 1971.
28. Bowen, E. J. and Brocklehurst, B., The fluorescence spectra of coronene and 1:12-benzoperylene at low temperatures, *J. Chem. Soc.*, 4, 3875, 1954.
29. Bowen, E. J. and Brocklehurst, B., The emission spectra of aromatic hydrocarbons in crystalline paraffins at −180°C, *J. Chem. Soc.*, 4, 4320, 1955.
30. Sidman, J. W., Vibrational analysis of the emission spectrum of coronene as a forbidden transition, *J. Chem. Phys.*, 23, 1365, 1955.
31. Dikun, P. P., Fine structured fluorescent spectra used for carcinogenic compound determination, *Vopr. Onkol.*, 6, 75, 1960; *Chem. Abstr.*, 55, 10557f, 1961.
32. Dikun, P. P. and Chushkin, S. G., The fluorescent spectral study of products resulting from smoking, *Vopr. Onkol.*, 5, 34, 1959; *Chem. Abstr.*, 54, 3682b, 1960.
33. Gorelova, N. D. and Dikun, P. P., Demonstrating the presence of 3,4-benzopyrene in human lung tissue, *Vopr. Onkol.*, 5, 161, 1959; *Chem. Abstr.*, 54, 1708i, 1960.
34. Shpol'skii, E. V. and Girdzhiyauskaite, E. A., Luminescence and absorption of pyrene and 3,4-benzopyrene in frozen solutions of normal paraffins, *Opt. Spektrosk.*, 4, 620, 1958; *Chem. Abstr.*, 52, 2781h, 1958.
35. Dikun, P. P., The detection of polycyclic hydrocarbons in smoked fish by means of fine structure of fluorescent spectra, *Vopr. Onkol.*, 11, 77, 1965; *Chem. Abstr.*, 62, 15349c, 1965.
36. Dikun, P. P., The appearance of polycyclic aromatic hydrocarbons and of other materials in polluted air by quasi-linear fluorescence spectra, (transl.), *J. Appl. Spectrosc. (USSR)*, 6, 130, 1967.
37. Dikun, P. P., Detection of the strong carcinogens 1,2:4,5- and 3,4:9,10-dibenzopyrene in the atmosphere, *Vopr. Onkol.*, 12, 90, 1966; *Chem. Abstr.*, 64, 14853d, 1966.
38. Dikun, P. P., Fine structure fluorescence spectra of the mono-methyl derivatives of 1,2-benzanthracene, *Vopr. Onkol.*, 7, 64, 1961 (British Library transl. RTS 8408).
39. Gurov, F. I. and Novikov, Yu. V., Fluorimetric spectrography of polycyclic aromatic hydrocarbons in snow and soil samples, (transl.), *Hig. Sanit. (USSR)*, 36, 409, 1971.
40. Florovskaya, V. N., Teplitskaya, T. A., and Pikovskii, Yu. I., Aromatic hydrocarbons in the rocks and minerals of hydrothermal deposits (as exemplified by the Darasun gold deposit in the eastern Transbaikal region), (transl.), *J. Appl. Spectrosc. (USSR)*, 3, 117, 1965.
41. Florovskaya, V. N., Teplitskaya, T. A., and Ovchinnikova, L. I., Distribution of aromatic polycyclic hydrocarbons in the sedimentary rocks of the Prikarabogaz'e, (transl.), *J. Appl. Spectrosc. (USSR)*, 4, 268, 1966.
42. Florovskaya, V. N., Vdovkin, G. P., Teplitskaya, T. A., and Zezin, R. B., Comparative characteristics of polycyclic aromatic hydrocarbons in carbonaceous chondrites, rocks and minerals of endogenic origin, *Meteoritika*, 26, 169, 1965; *Chem. Abstr.*, 65, 2009e, 1966.
43. Parker, C. A. and Hatchard, C. G., Photoreaction of benz(a)pyrene in solutions containing polymer, *Photochem. Photobiol.*, 5, 699, 1966.
44. Lavalette, D., Muel, B., Hubert-Habart, M., René, L., and Latarjet, R., Utilisation de l'excitation sélective de la fluorescence a 77°K pour l'analyse de mélange d'hydrocarbures polycycliques condensés, *J. Chim. Phys.*, 65, 2144, 1968.

45. Bogomolov, S. G., Pemova, F. D., and Kolosova, L. P., "Last lines" of the spectrum at various temperatures of 3,4-benzopyrene, dissolved in normal hydrocarbons, *Izv. Akad. Nauk SSSR*, 24, 725, 1960; *Chem. Abstr.*, 54, 22001g, 1960.
46. Il'ina, A. A. and Personov, R. I., Lime emission spectra of 1,12-benzoperylene and its identification in some natural products, (transl.), *Geochemistry (USSR)*, 11, 1089, 1962.
47. Muel, B. and Lacroix, G., Caractérisation et dosage du 3-4 benzopyrène par spectrophotométrie de luminescence à −190°C, *Bull. Soc. Chim. Fr.*, 5, 2139, 1960.
48. Dikun, P. P., The quantitative determination of small concentrations of 3,4-benzopyrene by means of the fine structure of the fluorescence spectrum, *Vopr. Onkol.*, 7, 42, 1961.
49. Personov, R. I., Quantitative determination of 3,4-benzopyrene on the basis of its linear fluorescence spectrum at 77 K, (transl.), *J. Anal. Chem. (USSR)*, 17, 503, 1962.
50. Prokhorova, E. K. and Znamensky, N. N., On the contents of 3,4-benzopyrene in paraffin of Soviet make, *Vopr. Onkol.*, 9, 72, 1963; *Chem. Abstr.*, 60, 5245g, 1964.
51. Shpol'skii, E. V. and Personov, R. I., The spectral analysis of organic compounds by emission using the low temperature line spectrum, (transl.), *Ind. Lab. (USSR)*, 28, 451, 1962.
52. Eichhoff, H. J. and Köhler, M., Identifizierung und Bestimmung polycyclischer, aromatischer Kohlenwasserstoffe durch Fluorescenzspektren fester Lösungen bei tiefen Temperaturen, *Z. Anal. Chem.*, 197, 271, 1963.
53. Personov, R. I. and Teplitskaya, T. A., Quantitative determination of some polynuclear aromatic hydrocarbons on the basis of their quasilinear fluorescence spectra, (transl.), *J. Anal. Chem. (USSR)*, 20, 1176, 1965.
54. Varshavskii, I. L., Shabad, L. M., Khesina, L. Ya., Khitrovo, S. S., Chalabov, V. G., and Pakhol'nikh, A. I., Determination of 3,4-benzopyrene in diesel exhausts from fluorescence spectra, (transl.), *J. Appl. Spectrosc. (USSR)*, 2, 68, 1965.
55. Jäger, J. and Lugrová, O., Determination of 3,4-benzopyrene in mixtures by means of fluorescence spectrography at a temperature of −197°C, *Chem. Zvesti*, 19, 774, 1965 (British Library transl. RTS 8582).
56. Jäger, J., Utilisation of quasilinear fluorescence spectra in analysis of polynuclear aromatic hydrocarbons, *Atmos. Environ.*, 2, 293, 1968.
57. Jäger, J. and Kassowitzová, B., Determination of 3,4-benzopyrene in drinking water, *Chem. Listy*, 62, 216, 1968.
58. Jäger, J. and Kassowitzová, B., The breakdown of 3,4-benzopyrene in water, *Cesk. Hyg.*, 13, 288, 1968.
59. Arabdize, A. A., A method for determining the purity of coronene and pentacene from their quasilinear luminescence spectra, (transl.), *J. Appl. Spectrosc. (USSR)*, 4, 180, 1966.
60. Florovskaya, V. N., Teplitskaya, T. A., and Personov, R. I., Quantitative investigation of polynuclear aromatic hydrocarbons in the organic matter of rocks of various origins, (transl.), *Geochemistry (USSR)*, 3, 419, 1966.
61. Danil'tseva, G. E. and Khesina, A. Ya., Use of quasilinear fluorescence spectra for the quantitative determination of 7,12-dimethylbenzanthracene (9,10-dimethyl-1,2-benzanthracene: DMBA) in complex mixtures, (transl.), *J. Appl. Spectrosc. (USSR)*, 5, 196, 1966.
62. Dikun, P. P., Krasnitskaya, N. D., Gorelova, N. D., and Kalinina, I. A., Assay of 3,4-benzopyrene in mixtures using sharp-line fluorescence, (transl.), *J. Appl. Spectrosc. (USSR)*, 8, 254, 1968.
63. Fedoseeva, G. E. and Khesina, A. Ya., Use of quasiline luminescence spectra for quantitative determination of several polycyclic hydrocarbons, (transl.), *J. Appl. Spectrosc. (USSR)*, 9, 838, 1968.
64. Kolyadich, M. N., Khesina, A. Ya., Shefer, S. S., and Yamskova, V. P., Formation of a carcinogenic benzopyrene (BP) hydrocarbon in industrial petroleum oils during their use, *Gig. Tr. Prof. Zabol.*, 15, 3, 1971.
65. Stepanova, M. I., Il'ina, R. I., and Shaposnikov, Yu. K., Determination of polynuclear hydrocarbons in the exhausts from chemical and petrochemical production, (transl.), *J. Anal. Chem. (USSR)*, 27, 1075, 1972.
66. Khesina, A. Ya. and Petrova, T. V., Use of quasi-linear luminescence spectra for the determination of several polycyclic aromatic hydrocarbons in mixed solutions and complex extracts, (transl.), *J. Appl. Spectrosc. (USSR)*, 18, 622, 1973.
67. Shabad, L. M. and Smirnov, G. A., Aircraft engines as a source of carcinogenic pollution of the environment. (Benzo[a]pyrene studies), *Atmos. Environ.*, 6, 153, 1972.
68. Shabad, L. M., Khesina, A. Ya., and Serkovskaya, G. S., Content of carcinogenic hydrocarbons in different industrial and natural products, in *Nekotorye Itogi Izucheniya Zagryazneniya Vneshnei Sredy Kantserogennymi Veshchestvami (Certain Results in the Study of Environment Pollution by the Carcinogenic Substances)*, Shabad, L. M., Ed., U.S.S.R. Ministry of Public Health, Moscow, 1972, 85; *Chem. Abstr.*, 79, 83042v, 1973.

69. Serkovskaya, G. S., Methods for investigation of various petroleums, petroleum oils and medicinal ointments based upon them, in *Nekotorye Itogi Izucheniya Zagryazneniya Vneshnei Sredy Kantserogennymi Veshchestvami (Certain Results in the Study of Environment Pollution by the Carcinogenic Substances)*, Shabad, L. M., Ed., U.S.S.R. Ministry of Public Health, Moscow, 1972, 91 (British Library transl. RTS 9330).
70. Lukasiewicz, R. J. and Winefordner, J. D., On the analytical utility of quasi-linear molecular emission spectra, *Talanta*, 19, 381, 1972.
71. Kirkbright, G. F. and de Lima, C. G., Use of Shpol'skii effect for the determination of trace amounts of polynuclear aromatic hydrocarbons, *Proc. Soc. Anal. Chem.*, 11, 55, 1974.
72. Kirkbright, G. F. and de Lima, C. G., The detection and determination of polynuclear aromatic hydrocarbons by luminescence spectrometry utilising the Shpol'skii effect at 77 K, *Analyst (London)*, 99, 338, 1974.
73. Kirkbright, G. F. and de Lima, C. G., Quasi-linear fluorescence and phosphorescence of some aromatic and heterocyclic compounds in tetrahydrofuran at 77 K, *Chem. Phys. Lett.*, 37, 165, 1976.
74. Gaevaya, T. Ya. and Khesina, A. Ya., Quantitative determination of polycyclic aromatic hydrocarbons in individual and multicomponent solutions from their quasilinear fluorescence and phosphorescence spectra, (transl.), *J. Anal. Chem. (USSR)*, 29, 1913, 1974.
75. Colmsjö, A. and Stenberg, U., The effect of n-alkane solvents on low temperature quasilinear fluorescence spectra of some polyaromatic hydrocarbons, *Chem. Scr.*, 9, 227, 1976.
76. Lai, E. P., Inman, E. L., Jr., and Winefordner, J. D., Conventional fluorescence spectrometry of polynuclear aromatic hydrocarbons in Shpol'skii matrices at 77 K, *Talanta*, 29, 601, 1982.
77. Yang, Y., D'Silva, A. P., and Fassel, V. A., Laser-excited Shpol'skii spectroscopy for the selective excitation and determination of polynuclear aromatic hydrocarbons, *Anal. Chem.*, 53, 894, 1981.
78. Colmsjö, A. and Stenberg, U., Temperature effects on resolution of quasi-linear fluorescence spectra of some polyaromatic hydrocarbons, *Chem. Scr.*, 11, 220, 1977.
79. Khesina, A. Ya., Smirnov, G. A., Ermakov, E. A., Knyazeva, A. A., and Yashin, Ya. I., Determination of polycyclic aromatic hydrocarbons in polluted environments from their quasi-linear luminescence spectra and by gas chromatography (transl), *J. Anal. Chem. (USSR)*, 33, 1559, 1979.
80. Colmsjö, A. and Stenberg, U., Vacuum sublimation of polynuclear aromatic hydrocarbons separated by thin-layer chromatography for detection with Shpol'skii low-temperature fluorescence, *J. Chromatogr.*, 169, 205, 1979.
81. Colmsjö, A. and Stenberg, U., Identification of polynuclear aromatic hydrocarbons by Shpol'skii low temperature fluorescence, *Anal. Chem.*, 51, 145, 1979.
82. Colmsjö, A. and Stenberg, U., The identification of polynuclear aromatic hydrocarbon mixtures in high-performance liquid chromatography fractions utilizing the Shpol'skii effect, in *Polynuclear Aromatic Hydrocarbons*, Jones, P. W., and Leber, P., Eds., Ann Arbor Science, Ann Arbor, Mich., 1979, 121.
83. Monarca, S., Causey, B. S., and Kirkbright, G. F., A rapid routine method for quantitative determination of benzo[a]pyrene in water by low temperature spectrofluorimetry, *Water Res.*, 13, 503, 1979.
84. Santoni, B. and Mandon, C., Dosage des hydrocarbures aromatiques polynucléaires dans les eaux et les sédiments par fluorimétrie à basse température, *Analusis*, 9, 259, 1981.
85. Paturel, L., Jarosz, F., Fachinger, C., and Suptil, J., Realisation d'un dispositif experimental pour le dosage des hydrocarbures aromatiques polycycliques par spectrofluorimetrie Shpol'skii a 10 K, *Anal. Chim. Acta*, 147, 293, 1983.
86. Drake, J. A. G., Jones, D. W., Causey, B. S., and Kirkbright, G. F., Shpol'skii luminescence spectroscopy of extracts of coal and coal-tar pitch, *Fuel*, 57, 663, 1978.
87. Colmsjö, A. L. and Östman, C. E., Selectivity properties in Shpol'skii fluorescence of polynuclear aromatic hydrocarbons, *Anal. Chem.*, 52, 2093, 1980.
88. Garrigues, P., Lamotte, M., Ewald, M., and Joussot-Dubien, J., Utilisation d'un cryogénérateur à cycle fermé pour l'analyse fluorimétrique des hydrocarbures aromatiques polynucléaires (HAP) en matrice Shpol'skii à 15 K. II. Application à l'analyse des méthylphénanthrènes dans un pétrole, *C.R. Acad. Sci. (Paris)*, 293, 567, 1981.
89. Ewald, M., Lamotte, M., Garrigues, P., Rima, J., Veyres, A., Lapouyade, R., and Bourgeois, G., Determination of isomers of monomethylphenanthrene extracted from petroleum by capillary gas chromatography coupled to mass spectrometry and by high resolution spectrofluorimetry in alkane crystals at a temperature of 15 K, *Advances in Organic Geochemistry 1981*, Bjøroy, M., Ed., John Wiley & Sons, Chichester, England, 1983, 705.
90. Rima, J., Lamotte, M., and Joussot-Dubien, J., Application of the Shpol'skii effect to quantitative analysis of monomethylphenanthrene isomers, *Anal. Chem.*, 54, 1059, 1982.
91. Rima, J., Lamotte, M., and Merle, A. M., Low concentration phenanthrene associations in Shpol'skii matrices, *Nouv. J. Chim.*, 5, 605, 1981.

92. Wehry, E. L., Experimental problems associated with the use of low-temperature glassy solvent matrices in phosphorometry, *Fluoresc. News*, 8, 21, 1974.
93. Garrigues, P., Ewald, M., Lamotte, M., Rima, J., Veyres, A., Lapouyades, R., Joussot-Dubiens, J., and Bourgeois, G., Low temperature spectrofluorimetry of complex mixtures of PAH, application to the analysis of isomeric PAH extracted from environmental samples (petroleum, marine sediments), *Int. J. Environ. Anal. Chem.*, 11, 305, 1982.
94. Ewald, M., Moinet, A., Saliot, A., and Albrecht, P., Identification of geochemical polycyclic aromatic hydrocarbons from terpenes by high-resolution Shpol'skii effect fluorescence spectrometry, *Anal. Chem.*, 55, 958, 1983.
95. Colin, J. M., Vion, G., Lamotte, M., and Joussot-Dubien, J., Quantitative trace analysis of polycyclic aromatic hydrocarbons by high-performance liquid chromatography and low temperature fluorimetry in Shpol'skii matrices at 4.2 K. Application to medicinal white oils, *J. Chromatogr.*, 204, 135, 1981.
96. Garrigues, P. and Ewald, M., Identification of monomethylated polycyclic aromatic hydrocarbons in crude oils by liquid chromatography and high-resolution Shpol'skii effect fluorescence spectrometry, *Anal. Chem.*, 55, 2155, 1983.
97. Lai, E. P., Jurgensen, A., Voigtman, E., and Winefordner, J. D., Low-temperature photoacoustic spectroscopy of polynuclear aromatic hydrocarbons in Shpol'skii matrices at 77 K, *Appl. Spectrosc.*, 36, 589, 1982.
98. Inman, E. J., Jr. and Winefordner, J. D., Low-temperature constant energy synchronous luminescence spectroscopy, *Anal. Chim. Acta*, 141, 241, 1982.
99. Nurmukhametov, R. N., Shpol'skii method in the spectroscopy of polyatomic molecules, *Russ. Chem. Rev.*, 38, 180, 1969.
100. Khesina, A. Ya., Khitrovo, I. A., and Fedoseeva, G. E., Spectra of phenols of benzo[a]pyrene in frozen crystalline solutions at 77 K and their use for the study of its metabolism, (transl.), *J. Appl. Spectrosc.*, 22, 644, 1975.
101. Pazhnina, S. V., Khesina, A. Ya., Édidel'shtein, B. A., and Gaevaya, T. Ya., Quantitative determination of indole, fluoranthrene, phenanthrene and chrysene from quasi-bright line phosphorescent spectra, (transl.), *Ind. Lab.*, 40, 1291, 1974.
102. Akhobadze, R. N., Melikadze, L. D., Teplitskaya, T. A., and Utkina, L. F., Possibility of identification of thiophene derivatives in complex organic mixtures by means of their quasiline luminescence spectra, (transl.), *J. Appl. Spectrosc.*, 27, 1010, 1977.
103. Colmsjö, A. L., Zebühr, Y. U., and Östman, C. E., Shpol'skii effect in the analysis of sulfur-containing heterocyclic aromatic compounds, *Anal. Chem.*, 54, 1673, 1982.
104. Garrigues, P., De Vazelhes, R., Ewald, M., Joussot-Dubien, J., Schmitter, J. M., and Guiochon, G., Identification of triaromatic azaarenes in crude oils by high-resolution spectrofluorimetry in Shpol'skii matrices, *Anal. Chem.*, 55, 138, 1983.
105. Woo, C. S., D'Silva, A. P., and Fassel, V. A., Characterization of environmental samples for polynuclear aromatic hydrocarbons by an X-ray excited optical luminescence technique, *Anal. Chem.*, 52, 159, 1980.
106. Colmsjö, A. L. and Östman, C. E., *Atlas of Shpol'skii Spectra and Other Low Temperature Fluorescence Spectra of POM*, University of Stockholm, Stockholm, Sweden, 1981.
107. Zaĭdel, A. N., Ostrovskaya, G. V., and Ostrovski, Yu. I., *Técnica y práctica de espectroscopia*, Editorial Mir, Moscow, 1979, chaps. 4, 10, and 12.
108. Causey, B. S., Kirkbright, G. F., and de Lima, C. G., Detection and determination of polynuclear aromatic hydrocarbons by luminescence spectrometry utilising the Shpol'skii effect at 77 K, *Analyst (London)*, 101, 367, 1976.
109. D'Silva, A. P., Oestreich, G. J., and Fassel, V. A., X-ray excited optical luminescence of polynuclear aromatic hydrocarbons, *Anal. Chem.*, 48, 915, 1976.
110. Woo, C. S., D'Silva, A. P., Fassel, V. A., and Oestreich, G. J., Polynuclear aromatic hydrocarbons in coal — identification by their X-ray excited optical luminescence, *Environ. Sci. Technol.*, 12, 173, 1978.
111. Svishchyov, G. V., Quasi-linear luminescence excitation spectra of pyrene, 3,4-benzopyrene, and coronene, (transl.), *Opt. Spectrosc.*, 18, 350, 1965.
112. Farooq, R. and Kirkbright, G. F., Detection and determination of polynuclear aromatic hydrocarbons by luminescence spectrometry utilising the Shpol'skii effect at 77 K. III. Luminescence excitation spectra, *Analyst (London)*, 101, 566, 1976.
113. Personov, R. I., Al'shits, E. I., and Bykovskaya, L. A., The effect of line structure appearance in laser excited fluorescence spectra of organic compounds in solid solutions, *Opt. Commun.*, 6, 169, 1972.
114. Vo-Dinh, T. and Wild, U. P., Laser excited luminescence of coronene in a Shpol'skii matrix, *J. Lumin.*, 6, 296, 1973.

115. Abram, I., Auerbach, R. A., Birge, R. R., Köhler, B. E., and Stevenson, J. M., Line narrowing and stimulated emission of perylene in n-octane at liquid helium temperature, *J. Chem. Phys.*, 61, 3857, 1974.
116. Dinse, K. P. and Winscom, C. J., Phosphorescent site selection spectroscopy of organic molecules in Shpol'skii matrices, *J. Lumin.*, 18/19, 500, 1979.
117. Brown, J. C., Edelson, M. C., and Small, G. J., Fluorescence line narrowing spectrometry in organic glasses containing parts-per-billion levels of polycyclic aromatic hydrocarbons, *Anal. Chem.*, 50, 1394, 1978.
118. Brown, J. C., Duncanson, J. A., Jr., and Small, G. J., Fluorescence line narrowing spectrometry in glasses for direct determination of polycyclic aromatic hydrocarbons in solvent-refined coal, *Anal. Chem.*, 52, 1711, 1980.
119. Chiang, I., Hayes, J. M., and Small, G. J., Fluorescence line narrowing spectrometry of amino polycyclic aromatic hydrocarbons in an acidified organic glass, *Anal. Chem.*, 54, 315, 1982.
120. Bykovskaya, L. A., Personov, R. I., and Romanovskii, Yu, V., Luminescence analysis of complex organic materials based on resolved line spectra produced by selective laser excitation, *Anal. Chim. Acta*, 125, 1, 1981.
121. Yang, Y., D'Silva, A. P., Fassel, V. A., and Iles, M., Direct determination of polynuclear aromatic hydrocarbons in coal liquids and shale oil by laser excited Shpol'skii spectrometry, *Anal. Chem.*, 52, 1350, 1980.
122. Yang, Y., D'Silva, A. P., Iles, M., and Fassel, V. A., Laser excited Shpol'skii spectrometry (LESS) for the selective excitation and determination of polynuclear aromatic hydrocarbons, *Proc. Soc. Photo-Opt. Instrum. Eng.*, 286, 126, 1981.
123. Yang, Y., D'Silva, A. P., and Fassel, V. A., Deuterated analogues as internal reference compounds for the direct determination of benzo[a]pyrene and perylene in liquid fuels by laser-excited Shpol'skii spectrometry, *Anal. Chem.*, 53, 2107, 1981.
124. Renkes, G. D., Walters, S. N., Woo, C. S., Iles, M. K., D'Silva, A. P., and Fassel, V. A., Determination of aromatic hydrocarbons in particulate samples by high-temperature extraction and Shpol'skii spectrometry, *Anal. Chem.*, 55, 2229, 1983.
125. Vershinin, V. I., Kuzovenko, I. V., Baranov, G. I., and Sizikov, A. M., Laser excitation of quasilinear low-temperature luminescence spectra for determining polyarenes, (transl.), *J. Anal. Chem. (USSR)*, 36, 677, 1981.
126. Parker, C. A., *Photoluminescence of Solutions*, Elsevier, Amsterdam, 1968, 245.
127. de Lima, C. G., The Application of the Shpol'skii Effect in Low Temperature Luminescence Spectrometry, Ph.D. thesis, University of London, London, 1975.
128. Stroupe, R. C., Tokousbalides, P., Dickinson, R. B., Jr., Wehry, E. L., and Mamantov, G., Low-temperature fluorescence spectrometric determination of polycyclic aromatic hydrocarbons by matrix isolation, *Anal. Chem.*, 49, 701, 1977.
129. Wehry, E. L. and Mamantov, G., Matrix isolation spectroscopy, *Anal. Chem.*, 51, 643A, 1979.
130. Wehry, E. L. and Mamantov, G., Low temperature fluorometric techniques and their application to analytical chemistry, in *Modern Fluorescence Spectroscopy*, Vol. 4, Wehry, E. L., Ed., Plenum Press, New York, 1981, chap. 6.
131. Tokousbalides, P., Wehry, E. L., and Mamantov, G., Observation of quasilinear fluorescence spectra (the "Shpol'skii effect") in matrix-isolated polycyclic aromatic hydrocarbons, *J. Phys. Chem.*, 81, 1769, 1977.
132. Maple, J. R., Wehry, E. L., and Mamantov, G., Laser-induced fluorescence spectrometry of polycyclic aromatic hydrocarbons isolated in vapor-deposited n-alkane matrices, *Anal. Chem.*, 52, 920, 1980.
133. Perry, M. B., Wehry, E. L., and Mamantov, G., Determination of polycyclic aromatic hydrocarbons in unfractionated solid solvent refined coal by matrix isolation fluorescence spectrometry, *Anal. Chem.*, 55, 1893, 1983.
134. Conrad, V. B. and Wehry, E. L., Laser-induced matrix isolation fluorescence spectrometry of methyl and methoxyl derivatives of benzo[a]pyrene, *Appl. Spectrosc.*, 37, 46, 1983.
135. Maple, J. R. and Wehry, E. L., Matrix isolation site selection in fluorescence spectrometry of polar derivatives of polycyclic aromatic hydrocarbon derivatives, *Anal. Chem.*, 53, 266, 1981.
136. Inman, E. L., Jr., Jurgensen, A., and Winefordner, J. D., Analytical figures of merit for low-temperature luminescence of polynuclear aromatic compounds, *Analyst (London)*, 107, 538, 1982.
137. Colmsjö, A., Zebühr, Y., and Östman, C., The effects of substituents on low-temperature quasilinear fluorescence spectra of some polyaromatic hydrocarbons, *Chem. Scr.*, 20, 123, 1982.
138. Lyons, J. W., Hardesty, P. T., Baer, C. S., and Faulkner, L. R., Structural interpretation of fluorescence spectra by automated file searching. Implementation and applications in liquid chromatography, in *Modern Fluorescence Spectroscopy*, Vol. 3, Wehry, E. L., Ed., Plenum Press, New York, 1981, chap. 1.

139. Vershinin, V. R., Ovechkin, A. B., and Teplitskaya, T. A., Computer-processed qualitative analysis of complex mixtures of polyarenes from their quasilinear luminescence spectra. Choice and use of characteristics lines, (transl.), *J. Anal. Chem. (USSR)*, 37, 959, 1982.
140. Pugovkin, M. M., Ol'khovik, G. A., and Vylegzhanin, O. N., System for the identification of individual components in mixtures on the basis of Shpol'skii spectra, (transl.), *J. Appl. Spectrosc. (USSR)*, 36, 536, 1982.
141. Wittenberg, M., Jarosz, J., and Paturel, L., Analyse quantitative des hydrocarbures aromatiques polynucleaires par spectrofluorimétrie Shpol'skii at 10 K: utilisation de la raie de mercure excitatrice diffusée par la matrice comme intensite luminescence de référence, *Anal. Chim. Acta*, 160, 185, 1984.
142. Wehry, E. L., Laser-induced low temperature fluorescence spectroscopy, *Trends Anal. Chem.*, 2, 143, 1983.
143. Hieftje, G. M., Low-cost tunable lasers, *Am. Lab. (Fairfield)*, 15, 66, 1983.
144. Hayes, J. M. and Small, G. J., Supersonic jets, rotational cooling, and analytical chemistry, *Anal. Chem.*, 55, 565A, 1983.