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LUMINESCENCE OF THE RARE-EARTH ELEMENTS AND ITS APPLICATIONS IN ANALYTICAL CHEMISTRY

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I. INTRODUCTION

Physical methods of analysis are now widely applied in analytical chemistry. In some cases, these are the only methods available: this is particularly true of the rare-earth elements (REE). These elements are so closely similar in chemical properties that analysis by conventional chemical methods becomes very difficult. Therefore they are usually analysed by spectroscopic methods, among which luminescence analysis is becoming increasingly important [1].

Analysis by emission spectroscopy [2], despite its generality, is also very difficult to apply to the REE, because the optical spectra of all the REE contain very many lines (of the order of thousands): unless the resolving power of the spectrograph is high enough, the lines of one element can be superimposed on those of another. The linear dispersion required is of the order of 1–2 Å.

Spectral analysis in the X-ray region of the spectrum is a better and more accurate method of analysis for REE, and is the most satisfactory method at present available. However, emission spectroscopic methods suffer from a relatively low sensitivity, reaching 10^{-3}% only in the most favourable case.

The similarity in chemical properties of the REE is known [3] to be due to the structure of the electron shells of the REE atoms: the inner 4*f* shell is progressively filled whilst the outer 5*s*, 5*p*, and 6*s* shells are already full, and this gives rise to the closely similar chemical properties.

The optical properties of the REE (light absorption and luminescence) are determined mainly by the 4*f* shell, and vary from element to element. Thus, they can be used to identify the individual elements. The screening of the inner 4*f* shell by the outer electron shells of the atom ensures that discrete spectra are obtained which are characteristic of these atoms, and makes the optical properties of the REE less sensitive to the surrounding medium.

II. LUMINESCENCE OF THE RARE-EARTH ELEMENTS

1. Luminescence of Pure Salts and Their Solutions

The optical properties of the REE are described in detail in a book by El'yashevich [3].

The absorption spectra of the REE, whether as crystals of the pure salts or in solution, are characterised by narrow bands in the infrared, visible, and ultraviolet regions of the spectrum. Wide bands, merging into a continuum, can be observed in the far ultraviolet. The discrete spectra of the REE ions are associated with quasi-forbidden transitions within the 4*f* shell: this is confirmed also by the small values of oscillator strength (*f*), of the order of 10^{-6}–10^{-8}. The continuous absorption in the ultraviolet must be ascribed to electronic transitions from the 4*f* shell to outer shells, which are strongly affected by the surrounding medium.

The luminescence spectra of REE situated in the middle of the group (Sm, Eu, Gd, Tb, Dy) also consist of a series of narrow bands. As in the case of the absorption spectra, this is due to transitions within the 4*f* shell. The lifetime in the excited state (τ) of these elements is high [4], of the order of 10^{-2}–10^{-4} s.

Systematic data on the absorption of REE ions in aqueous solution have been available since the work of Prandtl and Scheiner [5]. The absorption spectra show a systematic trend: the elements situated at the beginning and at the end of the REE group (except Ce and Yb) have absorption bands in the long-wavelength region of the spectrum, which gradually shift towards shorter wavelengths with elements lying near the middle of the group. Gadolinium absorbs only in the ultraviolet: this is because the ground level from which energy transitions occur during absorption shifts to a deeper position as we move towards gadolinium.

Unlike many other inorganic substances, which show luminescence only in the solid state, REE salts luminesce also in solution, retaining their characteristic spectrum.

The fluorescence and absorption spectra of triply charged REE ions, in solution or in the form of pure salts, were investigated systematically by Zaidel' and coworkers [6-9] and by many foreign workers [10-15].

The luminescence spectra of elements near the middle of the group (Sm, Eu, Gd, Tb, Dy) retain their line character even in solution. The elements at either end of the group have more diffuse spectra. In crystals, the bands are somewhat narrower, and are usually split into separate lines according to the strength and symmetry of the electric field in the crystal.

The structure of the luminescence bands, like that of the absorption bands, is slightly affected by the environment of the REE ion in solution or in the crystal (solvent effect in solution, and effect of crystal structure and of the anion in crystals). The pH of the medium has a particularly large effect on the luminescence. There is an optimum pH value for each system, giving maximum luminescence.

Both the upper and the lower energy levels are altered when the interaction between the ion and its surroundings increases. Since the upper levels usually suffer a greater shift, the spectrum is usually displaced towards longer wavelengths. The band structure is more clearly revealed at low temperatures, when both the resolution and the intensity of the bands are improved by the decreased energy fluctuations.

Luminescence can be induced in the REE by absorption in narrow spectral bands, and also by absorption in wide bands merging into a continuum in the ultraviolet region of the spectrum. The position of the luminescence bands is independent of the method of excitation (photoexcitation, or other kinds of excitation such as cathodic, X-rays, etc.). However, the intensity of bands can vary quite considerably, owing to the different quenching probabilities of different states of the ion, and also to the variation of the absorption coefficient of the ion with the wavelength of the exciting light.

Work on the luminescence of REE has been mainly directed, in recent years, towards interpreting the absorption and luminescence spectra of REE in pure salts and in solutions, and also towards studies of the effect of electric and magnetic fields on the energy state of the ions [16-30].

Many papers give new experimental results on the luminescent properties of REE. The absorption spectrum of promethium in solution (98% D_2O) has been determined [31] between 3000 and 8300 Å. It consists (Fig. 1) of various groups of lines, the most intense of which occur at the wavelengths 7347, 7019, 6838, 5679, and 3281 Å. The

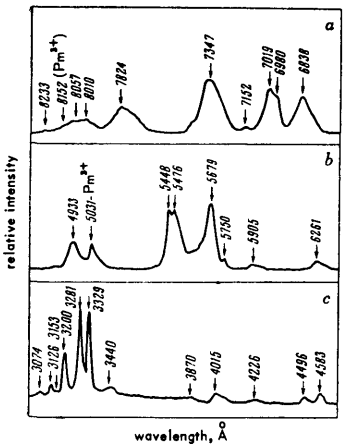


Fig. 1. Absorption spectrum of promethium in solution.

TABLE.

REE	Exciting source	Min. REE concn., %	λ, analytical, Å	Remarks
Ce	Fe spark	10^{-7}	3130—4070	aqueous solution[6]
Pr	Ni spark	$5\cdot10^{-3}$	6400	crystal phosphors[64]
Pr	cathode rays	$5\cdot10^{-5}$		crystal phosphors[88]
Nd	cathode rays	$5\cdot10^{-4}$	10800	crystal phosphors[88]
Sm	W spark	10^{-5}	5680 6100	crystal phosphors[91]
Eu	Fe spark	10^{-2}	5930 6160	aqueous solution[35]
Eu	cathode rays	10^{-4}		crystal phosphors[88]
Eu	Hg lamp	10^{-4}	6130	organic complexes[107]
Eu	W spark	10^{-5}	5930	crystal phosphors[91]
Gd	cathode rays	10^{-4}	3110	crystal phosphors[88]
Gd	W spark	10^{-6}	3130	crystal phosphors[91,92]
Tb	Ni spark	10^{-6}	5450	aqueous solution[7]
Tb	Hg lamp	10^{-3}	5450	organic complexes[107]
Tb	cathode rays	$5\cdot10^{-4}$		crystal phosphors[88]
Tb	Ni spark	10^{-5}	5430	crystal phosphors[69]
Dy	cathode rays	$5\cdot10^{-4}$		crystal phosphors[88]
Dy	Ni spark	10^{-4}	5760	crystal phosphors[69]
Ho	Ni spark	10^{-4}	5500	crystal phosphors[69]
Er	cathode rays	10^{-3}	5200—5500	crystal phosphors[88]
Tm	Ni spark	$5\cdot10^{-3}$	6540	crystal phosphors[69]
Tm	cathode rays	10^{-3}		crystal phosphors[88]
Yb		10^{-4}		crystal phosphors[128]

same authors have also reported[32] the luminescence spectrum of $PmCl_3$. This compound is self-luminous because of the high β activity of Pm. Under the influence of ultraviolet radiation its fluorescence increases as a function of the intensity of the exciting light. The fluorescence spectrum of $PmCl_3$ contains groups of lines around 4610, 4980, 5410, 5900, 6600, 7420, and 8300 Å. Several papers deal with the luminescent properties of Gd[33-35] and Tb[36-38].

The fluorescence of some REE can be observed in very dilute solutions[39-42] by using short-wavelength excitation (2000–3000 Å).

The Table gives the wavelengths of the most intense fluorescence bands, the minimum concentrations of the element, and the most effective excitation light sources for a number of REE ions in solution (Ce, Eu, Gd, Tb).

It should be noted that satisfactory results can be obtained only if the salts and the solvent (water, alcohol) are very pure. The Eu^{3+} ion is exceptional, because it does not fluoresce in a pure solution: SO_4^{2-} ions must be present to cause fluorescence of Eu^{3+}.

The intensity of fluorescence at low REE concentrations ($< 0.1\%$) is proportional to the amount of fluorescing element in solution. This property can be used for the quantitative estimation of REE in solution.

It can be seen from the Table that fluorescence analysis offers unsurpassed sensitivity for Ce, Gd, and Tb. The precision of the method depends very much on the procedure used to record the spectrum, and can be as high[41] as 1–2%.

2. Luminescence of Crystal Phosphors Activated by Rare-Earth Elements

Crystal phosphors[43,44] provide intense fluorescence with a characteristic line spectrum even with many of the other REE, *e.g.* Pr, Nd, Pm, Ho, Er, Tm. In this case the REE play the role of activators — a minor constituent, incorporated into the main substance, which determines the nature of the light emission from the phosphor. The photoluminescence of crystal phosphors can be induced either through light absorption by the activators themselves or by transfer to the activators of the radiant energy absorbed by the main constituent. Luminescence in these systems requires that the host material should be in the crystalline state: for this reason, the phosphors are subjected to heat-treatment. The host lattice for REE crystal phosphors may be provided by the oxides, sulphides, fluorides, sulphates, silicates, phosphates, tungstates, and molybdates of metals of Groups II–IV of the Periodic Table. REE phosphors having well-defined line spectra can be obtained with host materials in which the ionic radius of the cation is comparable with that of the activator. Under these conditions, activator ions can be introduced into the host crystal by isomorphous substitution. The most effective hosts for REE are found experimentally to be calcium tungstate and calcium fluoride.

The properties of crystal phosphors activated by REE, the features of their luminescence, and the nature of the luminescence centres form the subject of a continuing investigation by Feofilov[45-54], who has made a special study of Ca, Ba, and Sr fluorides, and by other workers[55-87].

Feofilov's work (based on the polarisation method) leads to the conclusion that large numbers of luminescence centres are present, and makes it possible to link the various types of centre with certain preparative conditions (in particular, the charge of the activating ion may vary according to the conditions of synthesis)[52,53]. The luminescence spectrum and the value of τ depend on the charge of the activator ion. Double charged REE ions, unlike the triply charged ions, are characterised by wide bands and low values[49,51,53] of $\tau(\sim 10^{-6}$ s).

A review by Feofilov[52] gives a chart of the spectral regions in which luminescence bands of the individual REE ions have been observed in crystals of fluorite CaF_2. This chart (Fig. 2) is reminiscent of Prandtl's scheme for the absorption spectra of the REE. The luminescence spectra also show some regularity, though possibly less marked, in the location of the bands corresponding to the various REE ions. For ions close to the beginning or the end of the REE group the luminescence spectra are displaced towards long wavelengths, whereas the luminescence of Gd occurs only in the far ultraviolet.

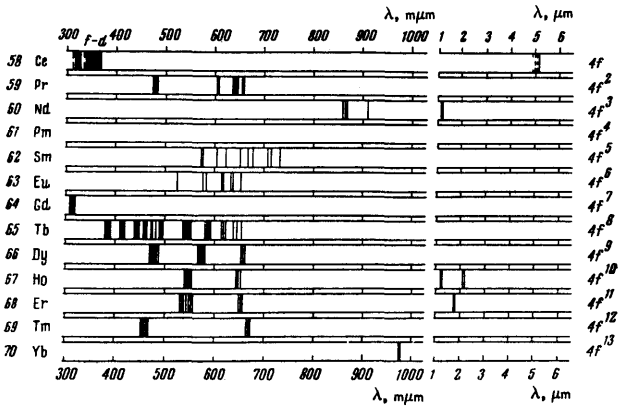


Fig.2. Schematic chart of the luminescence spectra of REE ions in CaF_2 crystals.

Many of the papers already mentioned[55,58,60] deal with the properties of phosphors based on the sulphides or oxides of alkaline earth metals activated by REE. There are also some papers[61,66,67] on the cathode luminescence of crystal phosphors activated by REE.

A paper by Trofimov[62] on the diffusion of REE activators in various crystals contains some very interesting results from the point of view of analytical chemistry. He puts forward a scheme (Fig. 3) showing the direction of diffusion of REE from one crystal to another — the "acceptor" crystal — at high temperatures. The best acceptors for REE are, according to Trofimov, ThO_2 and $CaMoO_4$, which become excellent crystal phosphors in the presence of REE. Fig. 4 shows the luminescence spectrum of one of the crystal phosphors based on ThO_2.

The luminescence spectra and intensity depend on both the nature and the concentration of the activator, and also on the nature of the substrate. The thermal history of the sample (temperature and time of heat-treatment) also plays an important role. The position of the bands in the luminescence spectrum of a phosphor activated by a given REE is practically independent of these factors, but the structure of the bands does vary.

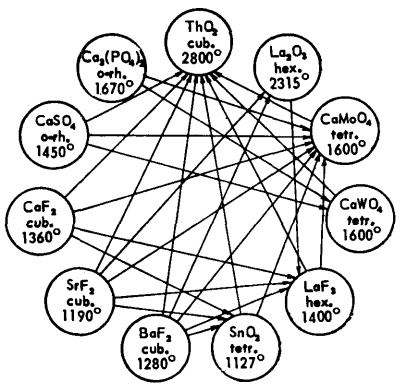


Fig.3. Scheme showing directional diffusion of activator when a mechanical mixture of two crystalline substances is heated (melting points indicated in circles).

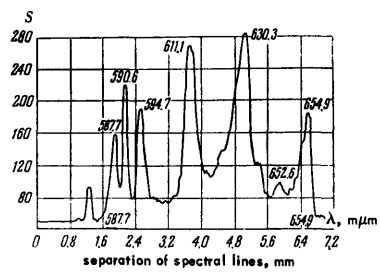


Fig.4. Luminescence spectrum of ThO_2–Eu.

The mode of splitting of the levels, which determines the type of spectrum obtained, is related to the crystal lattice and its symmetry, which in turn dictates the symmetry of the electric fields to which the luminescence centre is exposed.

The effect of the crystal lattice on absorption and emission spectra is shown in: (1) displacement of individual lines and groups of lines, related to changes in lattice parameters; (2) splitting of individual lines, determined by the symmetry of the surrounding electric field, *i.e.* by the symmetry of the crystal lattice of the host material of the phosphor (the number of components into which splitting occurs is higher the lower the symmetry of the field); (3) change in intensity of the lines for different crystal structures; (4) the appearance of new lines, caused by the superposition of vibrational levels of the host lattice itself upon the fundamental electronic transitions; and (5) line broadening, due to the possibility of an irregular arrangement of atoms in the crystal about the radiating ion, leading to random electric fields around the luminescence centres (non-isomorphous introduction of the activator into the lattice).

As was pointed out in the foregoing, these effects can be observed also in the pure salts, which can be regarded as phosphors with a high concentration of activator. The variation of luminescence spectra with the nature of the surroundings, which is an obstacle to the application of luminescence analysis in analytical chemistry, may be used to solve many problems in crystal chemistry, such as: (1) detection of incipient formation and decomposition of solid solutions; (2) identification of crystal lattice types; (3) recognition of polymorphic transformations; (4) demonstration of detailed features in the microstructure of crystals; (5) detection of microdefects in a crystal, and elucidation of their nature; (6) monitoring the formation of mixed crystals; (7) distinguishing the amorphous and the crystalline states of the material; and (8) the study of diffusion in the solid phase.

Several problems in crystal chemistry have been successfully solved by Trofimov[69] using the luminescence spectra of REE.

However, it is possible to use the luminescence spectra of REE for the analysis of these elements when present in the same external medium, *i.e.* when the REE are introduced into a host of a given composition under identical conditions.

Servigne published a series of papers[88] on luminescence analysis, in which he showed that the luminescence of REE can be detected at very low concentrations if calcium tungstate or molybdate is used as the host material. Some of his data on the minimum concentrations of REE activators

(Pr, Eu, Gd, Tb, Dy) are reproduced in the Table. For activator concentrations below 0.1% the luminescence intensity is usually proportional to the amount of activator (other conditions being equal). The luminescence of REE can therefore be used as a quantitative method of analysis either in liquid or in solid solutions (crystal phosphors).

It is important to remember, however, that impurities can have an effect, and that two or more activators can interact[70,84-87], when mixtures of elements are being determined. The computational difficulties of allowing for the various factors which affect the luminescence intensity have so far militated against the widespread use of the luminescence of crystal phosphors in quantitative analysis.

Very few papers on this topic have been published to date[89-96], but their importance is undeniable.

The determination of Gd, Eu, and Sm in thorium, and of Gd in beryllium, has been described[91,92]. The extremely bright luminescence of REE phosphors based on ThO_2 allows the determination of Gd, Eu, and Sm in thorium at the 10^{-5}% level with an accuracy of 20–50%. The high sensitivity (10^{-6}%) of the luminescence method of determining Gd in beryllium[92] was also achieved with the help of ThO_2, by utilising the phenomenon of the thermal diffusion of REE activators in crystals as indicated above.

Impurity effects can be avoided[89-92] by using the method of small additions. This consists in preparing a series of phosphors with the same host but containing different, known amounts of the activator element to be analysed. The intensities of the analytical line in the fluorescence spectrum are used to construct a graph, from which the unknown concentration of the element is read off. The additions should be comparable with the unknown concentration (assumed to be small) in order to avoid departures from linearity between fluorescence intensity and activator concentration.

The REE can be detected qualitatively in minerals by comparing the absorption or luminescence spectra of the samples with those of synthetic compounds of the same composition and containing REE additions. Work of this type has been reported by Feofilov[53], Przibram[97], and Trofimov[98].

Feofilov[53] and Przibram[97] have studied the nature of the coloration and luminescence of fluorite. Trofimov[98] has investigated the luminescence of zircons, and has been able to show that the line spectra in the visible region and in the ultraviolet are due to the presence of Dy and Gd respectively.

These papers[53,88-98] clearly illustrate the way in which the luminescence of crystal phosphors can be used in analytical chemistry. The method is suitable, in principle, for the analysis of all REE: however, the host crystal of the phosphor must be chosen so as to give maximum luminescence of the REE activator if the highest sensitivity is desired.

A disadvantage of the method is its great laboriousness, arising mostly from the need to exclude impurities, which entails complicated chemical manipulation.

Furthermore, as in the case of pure salts and solutions, short-wavelength ultraviolet radiation provides the most effective excitation of the luminescence of REE phosphors. Thus, the excitation source must be a spark with suitably chosen electrodes, which adds to the difficulty of the analysis.

Some authors have used a rapid method of preparing[93,95,99,100] REE crystal phosphors, by means of borax or NaF beads. However, the bead method has a much lower analytical precision.

3. Luminescence of Inner Complexes of Rare-Earth Elements

Organic inner complexes of the REE, which have recently been discussed in a number of papers[101-123], are of considerable interest. These investigations primarily aim to identify the mechanism whereby the energy of the exciting light is transferred from the organic part of the complex to the REE ions.

The organic compounds on which REE inner complexes are based absorb strongly in the range 200–400 mμm. When the complex is formed the absorption spectrum shifts a little further in the direction of longer wavelengths. Irradiation of some REE complexes (Eu, Sm, Tb, and Dy) in the near ultraviolet (*e.g.* $\lambda = 365$ mμm) produces strong luminescence of the REE, caused by transfer to the REE of the radiant energy absorbed by the organic part of the complex. Kuznetsova[107] has shown that the efficiency of energy transfer is high at low temperatures, when the probability of radiationless transitions is small.

The photoluminescence spectra of REE inner complexes (Fig. 5) retain a discrete structure and are not substantially different from the spectra of simple salts of these

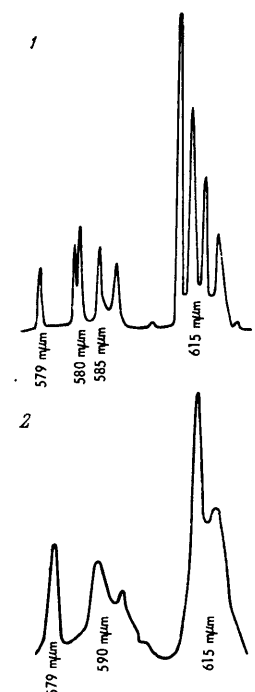


Fig.5. Luminescence spectra of the crystalline complexes of europium with:
1) ethylenediamine-2-hydroxy-naphthaldehyde;
2) ethylenediamine-5-nitrosalicyl-aldehyde.

elements in the crystalline state. The energy distribution in the spectrum and the type of splitting depend on the nature of the organic ligand.

The inner complexes exhibit luminescence both in the crystalline state and in solution provided that the resonance level of the REE ion is the lowest excited level of the whole system (Fig. 6), since only thus can energy transfer take place from the organic ligand to the REE ion. The resonance level of the Eu^{3+} ion is situated below all possible energy states of the complex, and therefore its spectrum is observed in the emission of practically every one of the complexes investigated, in solution as well as in the crystalline state, whereas the Gd^{3+} ion is not excited in any of the complexes because its resonance level is too high.

Since the energy state of the ion varies somewhat with the surrounding medium, it is sometimes found that the ions fluoresce only under certain conditions. For example, Sm, Tb, and Dy show luminescence only in some complexes. Samarium luminesces satisfactorily when complexed with ethylenediaminesalicylaldehyde. The luminescence of Tb can be observed by complexing it with phenyl salicylate (salol), the resulting complex luminescing only in solution. For Dy the complexes with *o*-phenanthroline and 2,2′-bipyridyl can be used. These latter complexes can be employed for the simultaneous analysis of all four REE elements mentioned above, including Sm. When Pr, Nd, Er, Ho, Tm, and Yb are present in complex compounds, emission occurs in the infrared.

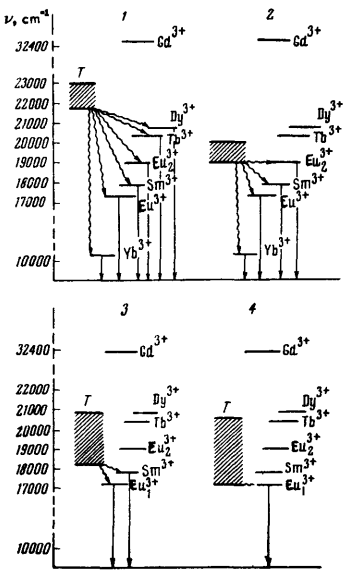


Fig. 6. Energy diagram showing how the energy of the exciting light is transferred from the organic ligand to the REE ion (the wavy arrows tentatively denote energy transfer from the lower level of the excited state of the organic ligand *T* to an excited level of an REE ion), energy being transferred to:
1) all the ions except Gd^{3+};
2) only Eu_2^{3+}, Sm^{3+}, and Yb^{3+};
3) only Sm^{3+} and Eu_1^{3+};
4) only Eu_1^{3+}.

In most cases, the luminescence of complexes can be observed only at low temperatures: only Eu gives good luminescence at room temperature. The work of Poluektov and coworkers [120,121] has shown that the luminescence intensity of REE can be enhanced by using ternary complexes with two different ligands able to transfer energy to the REE ion. Inner complexes of REE are easy to prepare, and the use of these materials therefore simplifies the luminescence analysis of REE, particularly since their luminescence can be excited by long-wavelength ultraviolet radiation from a mercury lamp.

The sensitivity of the method is fairly high, allowing, for example, Eu and Tb to be determined down to 10^{-4}% and 10^{-3}% respectively.

Papers on the use of the luminescence of REE complexes for analysis are not very numerous [119-123], but they provide adequate examples.

Neunhoeffer [124] has described an entirely different method of observing the luminescence of REE. The element to be analysed is mixed with calcium oxide, and the mixture is introduced into a hydrogen flame: strong luminescence is excited by the slow electrons present in the hydrogen flame. This procedure makes it possible to observe the luminescence of elements such as Y and La, which do not normally luminesce. The method is very sensitive, the author claiming that luminescence can be observed even at a concentration of Y as low as 10^{-6}%.

We may conclude, therefore, that the luminescence analysis of REE has an important role to play. In spite of some unfavourable features (such as the need to remove interfering impurities), the luminescence method for the analysis of REE merits close attention. With some elements (Eu, Sm, Gd, Tb, Dy), whose luminescence is very easily observed in nearly all the examples discussed in the foregoing, the procedure is already clear enough, and only remains to be introduced into everyday practice. For the other elements, further work is needed to find the simplest and most effective ways of observing the luminescence.

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GAS–LIQUID CHROMATOGRAPHY OF LIPIDS

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I. INTRODUCTION

Lipids and their component aliphatic alcohols, aldehydes, and acids form one of the most complex groups of naturally occurring compounds; for this reason, over the past few decades workers in many countries have used various types of chromatography such as adsorption, displacement, partition, and reversed-phase chromatography to study these compounds. Our ideas on the structure and metabolism of lipids in the living organism have been greatly extended by the use of these methods. However, there are many disadvantages associated with their use in lipid chemistry: much time is required to get a satisfactory separation, the analysis is not sufficiently reproducible, it is laborious, the distribution parameters for unsaturated and saturated lipids overlap, etc.

In the search for methods of effectively separating complex mixtures of lipids from the animal body, that sometimes contain as many as 60 components, the English biochemists James and Martin discovered in 1952 an entirely new type of chromatography, gas–liquid chromatography[1]. In this method separation of the mixture is based on the different distribution of the components between two phases, a stationary liquid phase supported on a solid carrier forming