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TWENTY YEARS OF THIN-LAYER CHROMATOGRAPHY

A REPORT ON WORK WITH OBSERVATIONS AND FUTURE PROSPECTS

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CONTENTS

1. INTRODUCTION

The first work with the title "thin-layer chromatography" (TLC) appeared in 1956[1]. It described a simple procedure for preparing very thin layers and reported the influence of layer thicknesses from 20 to 340 μm. It was found, using silica gel, that layers permitting fast flow and yielding good separation could be obtained only when the grain size lay mainly between 1 and 5 μm. Thus was the decisive step taken in chromatography for the transition from the relatively coarse-grained aluminium oxides used hitherto in the Tswett column chromatography to the very fine adsorbents with a narrow range of grain size (Fig. 1).

The real breakthrough in the method came with a second publication in 1958, in which standardization, detection, documentation and applications were described[2]. In the same year, the basic kits for thin-layer chromatography (Desaga, Heidelberg, G.F.R.) and silica gel G according to Stahl for TLC (Merck, Darmstadt, G.F.R.) were presented at the ACHEMA exhibition of chemical equipment at Frankfurt. It was already clear at that time that the method involved essentially adsorption chromatography on "open columns". The first applications were therefore principally in the domain of lipophilic compounds (Table 1). The existing rules of thumb of adsorption chromatography could be taken over and the relationships displayed in a "triangular scheme" (Fig. 2)[5].

The chromatography of polar, hydrophilic substance mixtures remained the preserve of paper chromatography (PC) for some time. In 1961, we were able to

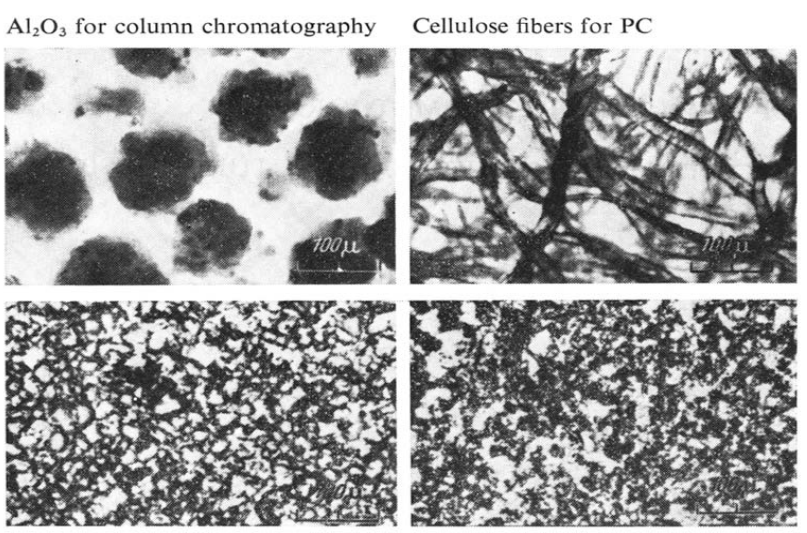

Fig. 1. Comparison of differences between the adsorbents for classical column chromatography and paper chromatography (above) and the fine adsorbents with a narrow range of grain size introduced for TLC (below).

extend the use of TLC to hydrophilic materials, as described in four publications. It could be shown that mixtures of sugars[8], heart glycosides[11] and numerous other hydrophilic plant components[10] were better and more rapidly separable by TLC than by PC. These publications recommended the use of TLC in trace analysis and demonstrated that amounts down to 0.005 µg, *i.e.*, 5 ng of, for example, certain indole derivatives such as heteroauxin, could be detected[9]. Nanogram-scale TLC had thus already come into existence at that time and, further, only short runs were required for trace analysis. This and much else is often forgotten today, or at least overlooked as a result of a lack of awareness of the literature. So many publications had appeared by 1962 that a team of specialists was able to bring out the first laboratory handbook on TLC[13]. The number of yearly publications increased exponentially, and 5 years later, the second, greatly expanded edition of the handbook, with *ca.* 1000 pages, appeared[24].

2. SPECIAL WORKING TECHNIQUES

In the first decade of TLC, we extended its application to virtually all types of mixtures and also devoted special attention to working techniques. Thus, the circular and wedged tip techniques and simple equipment for carrying them out were described in 1958[3]. This method, known from PC, is of particular interest through the apparent elimination of longitudinal diffusion of the spots which are formed into small bands as a result of the radial movement of the solvent. We recommended this "ring chromatography" for rapidly establishing the best solvent, for instance. Stepwise development was described for separating mixtures of substances with widely differing polarities[4]. Another study was of the influence of the degree of saturation of the separating chamber, with subsequent introduction of the so-called chamber saturation. Along with this, the sandwich chamber (S-chamber) was developed with the tubular

TABLE 1

LIPOPHILIC SUBSTANCE CLASSES CHROMATOGRAPHED BY STAHL AND CO-WORKERS (1957–1977)

Class of substance	*References*
Alkaloids	1, 18, 25, 27, 51, 53
Acids, organic	48
Anthraquinone derivatives	62
Azulene derivatives	1
Balsams	3
Calamus oils	7
Cannabinoids	59
Capsaicin	36
Carotinoids	4, 14
Chamomile oils	32
Colour indicators	18
Coumarin derivatives	54
Daucus oils	17
Drugs, hallucinogenic	46
Dyes, lipophilic	4
Ergot alkaloids	4
Essential oils	2, 3, 7, 17, 20, 28, 32, 37
Flavonoids	52
Flavours	37
Glechoma constituents	39
Glycols	48
Iodine compounds, organic	16
Lipids, ointments, etc.	60, 61
Morphactines	34
Opium alkaloids	27
Peroxides, organic	2
Pesticides	35
Phenols and derivatives	4, 42, 43, 49, 59
Phloroglucinolbutanones	12, 15
Phthalids	23
Picrocrocin	33
Polyamines	48
Preservatives	35
Pyrethrins	6, 21
α-Pyrone derivatives	45
Resins	3
Safranal	33
Saponins	41
Steroids	5
Tars	3
Terpene alcohols	20
Tropa alkaloids	25
Tyrosine derivatives	16
Valepotriates	31
X-ray contrast agents	16

trough. In 1960, the two-dimensional SRS (separation–reaction–separation) technique was described for investigating photooxidation[6]. This is a simple but very useful method, later termed "reaction chromatography", in my opinion a somewhat unfortunate description.

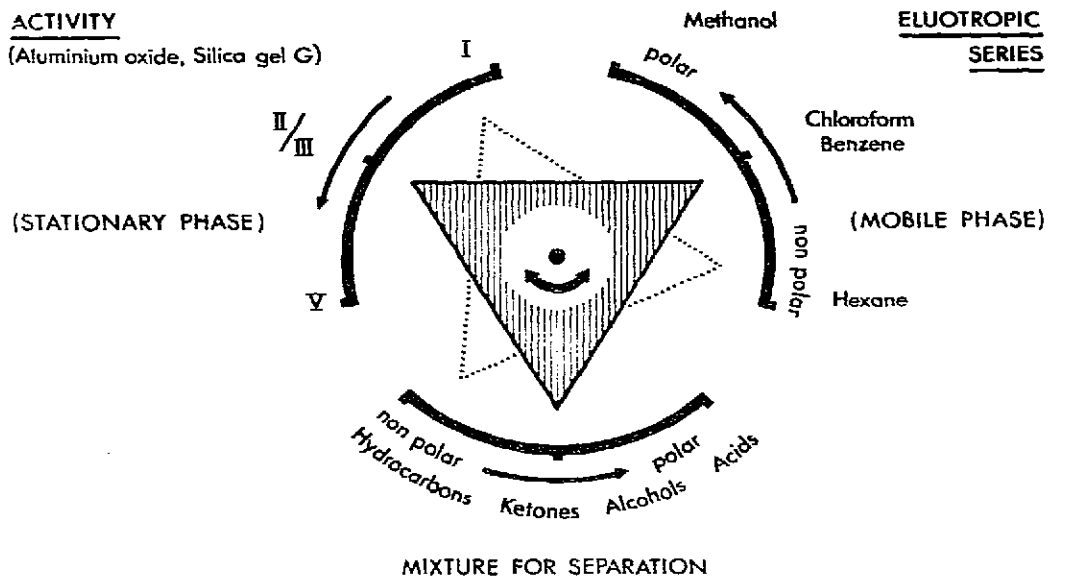

Fig. 2. Triangular scheme showing the close relation of the three variable quantities in chromatography, demonstrated on the example of adsorption chromatography. One has to imagine that the central triangle is turnable with one tip directed towards the mixture.

The so-called gradient-TLC[19] brought a climax and genuine step forward in 1964. Gradient layers can be easily and rapidly prepared using a special gradient spreader. Three different separating surfaces are available on a gradient layer, in contrast to the one type on the usual uniform layers (Fig. 3). Development can be carried out at right-angles to the gradient (T-gradient technique) or in two different directions along the line of the gradient. A few years later we succeeded in preparing defined pH-gradient layers. Chromatography on these of, *e.g.*, basic, amphoteric or acidic substances, perpendicular to the gradient, furnishes typical curves which are sometimes even substance-specific (Fig. 4). These can serve for the identification of individual compounds in an unknown mixture. The possibilities of application of such gradient layers have by no means been exhausted. It does seem, however, that most workers are still content with the uniform layers or avoid preparing gradient layers, simple though that is.

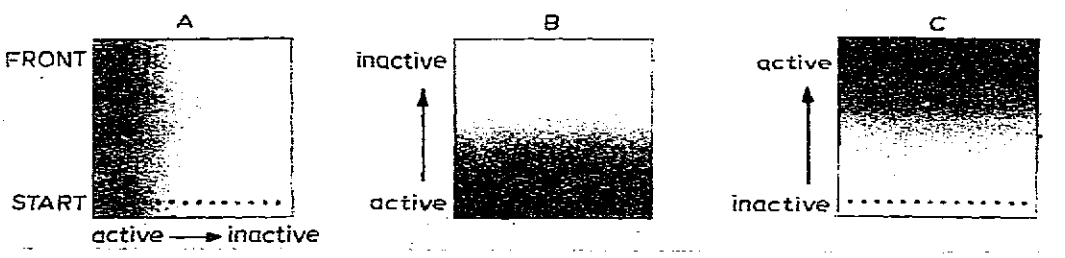

Fig. 3. Three different separating surfaces available on a gradient layer. Development is possible (A) at right-angles to the gradient and (B) and (C) along the line of the gradient, in the example from active to inactive or from inactive to active.

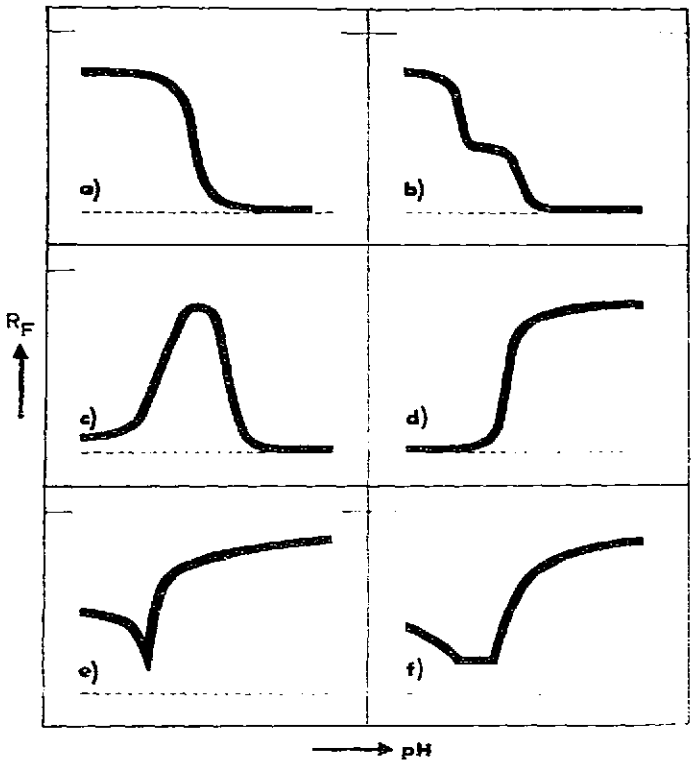

Fig. 4. Typical curve shapes obtained in pH–T-gradient chromatography. (a) Monobasic acid; (b) dibasic acid; (c) amphoteric compounds, such as anthranilic acid; (d) monoacidic amine; (e) opium alkaloids; (f) Tropa alkaloids.

We regard R_F values in TLC only as guide values and therefore showed an early interest in methods for identifying substances present in only microgram amounts. The techniques for transferring such small amounts from one method to another raised problems here. The possibilities were summarized in 1966 in a scheme (Fig. 5) and a "strategy for substance identification" was laid down[22]. At this time our experiments in collaboration with the firm of Zeiss for the direct quantitative evaluation of thin-layer chromatograms were concluded and production of the chromatogram–spectrophotometer began. A former pupil, Professor H. Jork, has continued detailed studies of quantitative evaluation.

3. STANDARDIZATION AND TERMINOLOGY

I recognised early the necessity for standardization of the TLC method. This began with the plate size (20 × 20 cm), the length of run, the position of the starting points, chamber saturation and, not to be forgotten, the standardization of adsorbents with the help of test mixtures. This enabled work to be performed everywhere under the same conditions, in contrast to that with other chromatographic and electrophoretic methods; the results obtained were therefore comparable. This yielded great

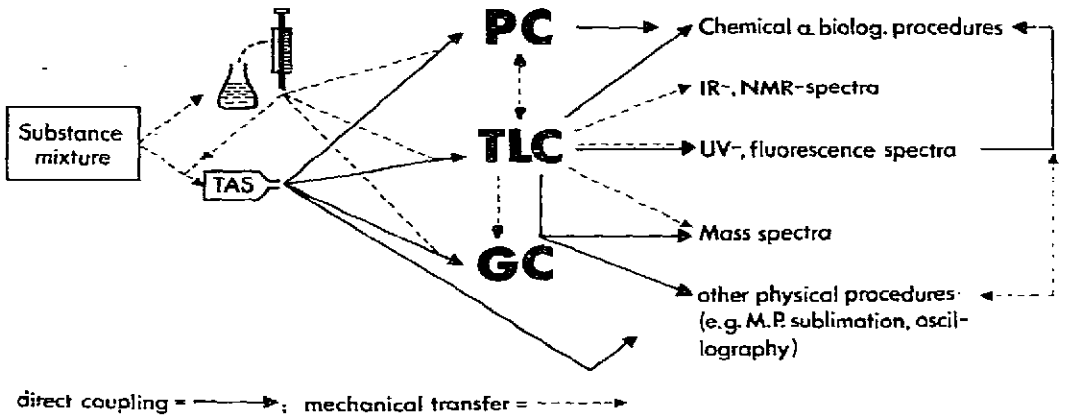

Fig. 5. Possibilities of coupling and combination of TLC and other methods.

advantages for the manufacturer of TLC equipment and especially for the user. International understanding demanded also that we concerned ourselves with terminology and definitions[26]. As a result, TLC rapidly found a place in legally binding test procedures, *e.g.*, in pharmacopoeias. Suggestions were made for preparing such monographs and numerous procedures were devised for drug characterization in the European and German Pharmacopoeias[25].

4. THE SECOND DECADE OF THIN-LAYER CHROMATOGRAPHY

In the second decade of TLC, after 1967, the emphasis of our work lay at first on the micro-extraction of substances from complex samples and the direct transfer to the thin layer. Experience had already shown that the preparation of the sample, *i.e.*, extraction with liquid, filtration, evaporation, redissolution and application often took much longer than the TLC itself and, moreover, usually led to considerable substance losses. Hence, we sought coupling procedures that would avoid this preliminary work and permit largely quantitative transfer to TLC.

In addition, we were interested in the problem of characterization, *i.e.*, the analysis of natural and synthetic polymeric material with the help of TLC. At the time, it was not possible to detect cellulose, lignin, polyphenols or proteins in plant drugs: nor could analyses of synthetic polymers, a vast domain, be performed by TLC.

5. TAS PROCEDURE

As already stated, the preliminary preparation of plant material for subjection to TLC is often the most time-consuming part of the whole procedure. Consequently, we made many attempts to develop a direct extraction and transfer method. Stimulated by the work on microsublimation by Kofler and Fischer in the 1930s, we first tested out thermal extraction procedures. Step by step this led to the TAS procedure, patented in 1967.

The sample, usually 1–10 mg, is placed in a glass cartridge, which is closed at

one end, the other end being drawn out to form a capillary. The cartridge is then placed in the TAS oven (Fig. 6) which has been heated to a given temperature (up to 350°). The volatile substances pass as a jet through the capillary directly on to a thin layer positioned 0.1–0.5 mm from the capillary exit. There they form the starting points on the thin-layer plate and can be submitted to the usual development.

The possibilities of application in various fields were demonstrated in twelve publications in 1968 and subsequent years. Special studies were devoted to the procedures taking place during extraction, to optimization and to quantitative aspects. The TAS method was quickly adopted in many laboratories and is used widely both in industry and in pharmacognosy teaching for rapid extraction coupled with TLC.

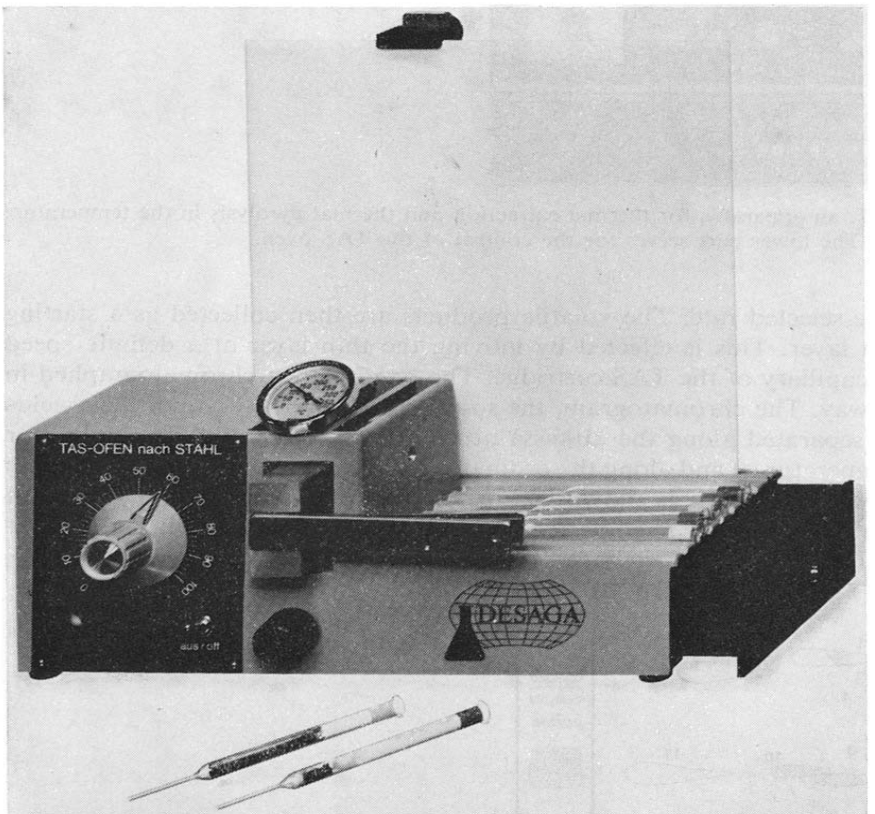

Fig. 6. TAS oven for thermal extraction and for direct transfer of the sample to the thin layer.

6. THERMOFRACTOGRAPHY[40]

A logical further development of the TAS procedure led first to band condensation of the substances for preparative recovery and later to the so-called thermofractography (TFG). The apparatus for the latter was called the TASOMAT (Fig. 7). A suitable controlling mechanism was developed for regulating and controlling the temperature, the rate of heating and the final temperature. In the TASOMAT, the temperature of a few milligrams of sample is raised linearly from room temperature

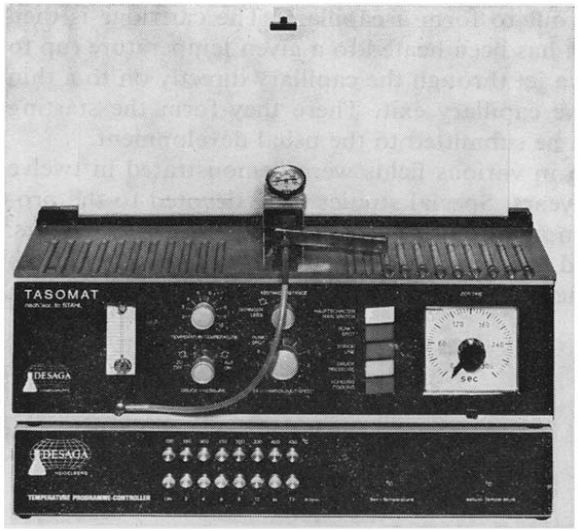

Fig. 7. TASOMAT, an apparatus for thermal extraction and thermal pyrolysis in the temperature gradient 50–450°. The lower part serves for the control of the TAS oven.

to 450° at a pre-selected rate. The volatile products are then collected as a starting band on a thin layer. This is effected by moving the thin layer at a definite speed across the exit capillary of the TAS cartridge. The band is then chromatographed in the customary way. The chromatogram, the so-called thermofractogram, then yields the substances separated along the abscissa according to their volatility (boiling or sublimation temperatures) and along the ordinate according to their chromatographic behaviour. A typical example is shown in Fig. 8. This fractional thermal extraction is in principle a distillation or sublimation in a carrier gas. This is the first time that

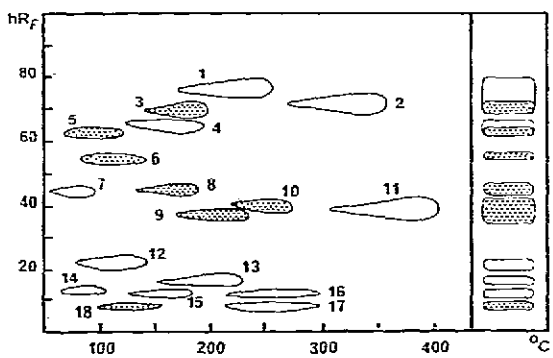

Fig. 8. Typical thermofractogram, with the substances separated along the abscissa according to their boiling temperatures and along the ordinate according to their chromatographic behaviour. On the right: a normal application of samples in fluid. 1 = Squalene; 2 = cholesteryl stearate; 3 = sulphur; 4 = guaiazulene; 5 = biphenyl; 6 = anethole; 7 = 1,8-cineole; 8 = benzyl benzoate; 9 = benzyl cinnamate; 10 = dioctyl phthalate; 11 = triolein; 12 = eugenol; 13 = oleic acid; 14 = menthol; 15 = palmitic alcohol; 16 = wool wax aliphatic alcohols; 17 = wool wax sterols; 18 = vanillin.

microgram amounts of many substances with high boiling or sublimation points were transferred directly on to a thin layer. The separation effect corresponds roughly to that of a distillation under a pressure of 0.1 mmHg. This is shown in particular by our work on the rapid analysis of lipid mixtures, *e.g.*, of ointments, suppositories and cosmetic preparations such as creams and lipsticks[58,60,61]. Such analyses previously used to take several days, whereas one now has a picture of the composition within an hour.

Basically, all substances which can be subjected to gas chromatography are amenable to thermal separation by TFG. Naturally, the procedure does not apply to a number of polar and non-volatile substances. However, during TFG these undergo thermal decomposition within a particular temperature range, that is, pyrolysis or, better, thermolysis, occurs. Definite fragmentation products are thus obtained which can serve for identification on the thermofractogram (fingerprint). For example, we have had good success in distinguishing different lignins[42]. Fig. 9 shows the difference between thermolysates from beech and pine lignins. The characterization of tannins by means of TFG was also valuable. These investigations form the basis for extensive analyses of leather samples[43]. Using only a few milligrams of leather sample, it is possible to show how the tanning was carried out. After these encouraging results we turned to the investigation of plastics and were able to carry out the rapid identification of condensation polymers (nylon and Perlon types), phenol resins, vinyl polymers and also of plasticizers and other additives[48,49,63].

In further studies, we then performed classical thermal reactions in the temperature gradient of the TFG. This had the advantage that such reactions can be

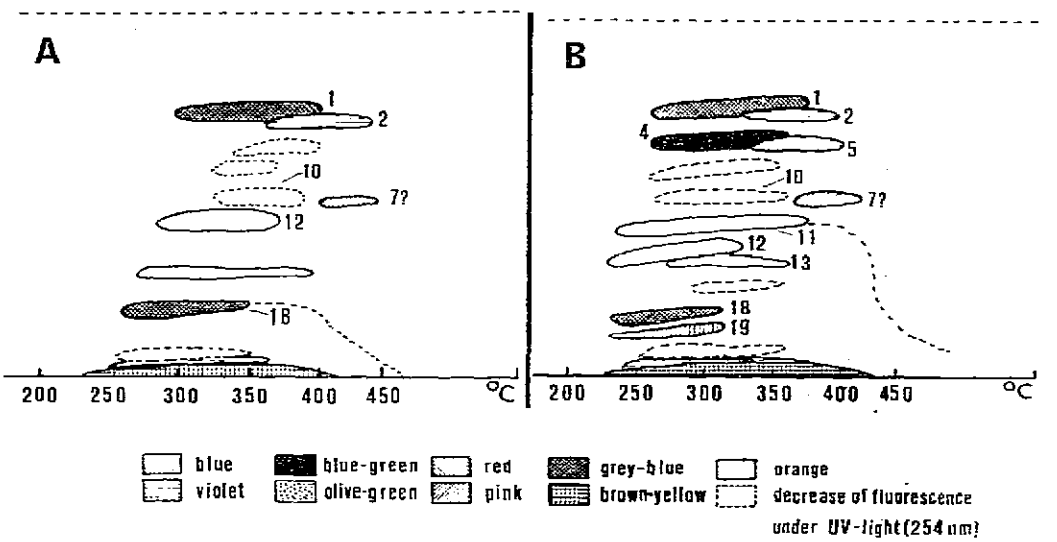

Fig. 9. Thermofractograms of liguins. (A) Spruce lignin. Colours are obtained after spraying with Fast Blue Salt B; only the corresponding guaiacyl derivatives are obtained. 1 = Vinylguaiacol; 2 = guaiacol; 10 = vanillin; 12 = coniferaldehyde; 18 = coniferyl alcohol. (B) beach lignin. Besides the guaiacyl compounds the corresponding syringyl derivatives are obtained. 4 = 4-Vinyl-2,6-dimethoxyphenol; 5 = 4-ethyl(or methyl)-2,6-dimethoxyphenol; 11 = syringaldehyde; 13 = sinapaldehyde; 19 = sinapyl alcohol.

TABLE 2

TYPICAL CONDITIONS FOR THERMAL REACTIONS AND DEHYDROGENATIONS COUPLED WITH TLC

The optimal conditions in the given ranges vary from substance to substance.

Method	*Sample (μg)*	*Reaction partner or catalyst*	*Temperature (°C)*
Zinc dust distillation	5– 50	200–300 mg of Cu-activated zinc dust	350–450
Sulphur dehydrogenation	50–100	10 mg of sulphur dehydrogenation mixture	160–220
Selenium dehydrogenation	100–200	20–30 mg of selenium dehydrogenation mixture	250–320
Catalytic dehydrogenation	20–100	25 mg of Pd–$BaSO_4$ (10%)	250–350

conducted with microgram amounts, as found, for example, in chromatographic zones. All of the substances formed are found on the corresponding thermofractograms and this enables the course of the reaction to be recognized. Work in the ultramicro region was carried out on dehydrogenation with sulphur and with selenium, catalytic dehydrogenation and zinc dust distillation. A summary is given in Table 2 of the necessary amounts, catalysts and temperatures[44,47,50].

These techniques can be regarded also as carbon-skeleton TLC, analogous to that in gas chromatography. A review of thermal work coupled with TLC was prepared for the occasion of the ACS award in chromatography[55].

Labile natural products are, however, not ideal subjects for separation using thermal methods. We thus sought less drastic extraction methods which permitted direct coupling with TLC; this led us to the supercritical gases.

7. FLUID EXTRACTION COUPLED WITH THIN-LAYER CHROMATOGRAPHY

The solubilities of many substances in supercritical gases increase as the pressure is raised. It was therefore of interest to employ such gases under pressure in the compressed state, *i.e.*, in the supercritical region, for extraction. The problems of coupling with TLC could be circumvented by pressure release through very fine capillaries (I.D. 50 μm). The gas stream exits through the fine capillary and impinges directly on to the thin layer. The layer is moved relatively rapidly back and forth and thus collects a starting band of the extracted substances. Normally, 1 Nl* gas is used per pressure stage for extraction. The thin layer is then displaced and a further extraction performed with 1 Nl at a correspondingly higher pressure, etc. We first developed an apparatus for this new type of coupling procedure[56] and then carried out many experiments on model mixtures to test their extractability. We were able to establish rules of thumb which enabled the extractability to be estimated from the structural formulae[57]. At first, we worked in the pressure region up to 500 bar and subsequently extended this to 2500 bar[64]. Supercritical carbon dioxide was used and also, especially for alkaloid extraction, supercritical nitrous oxide[65]. A typical fluid extraction–thin-layer chromatogram (FE–TLC) is shown in Fig. 10.

This work on fluid extraction concluded for the time being our efforts to find suitable coupling procedures with TLC. The scheme in Fig. 11 summarizes our endeavours in this domain during the second decade of TLC. Various means of extracting sample components and transferring them directly to TLC are now available.

* Nl = Normal liter.

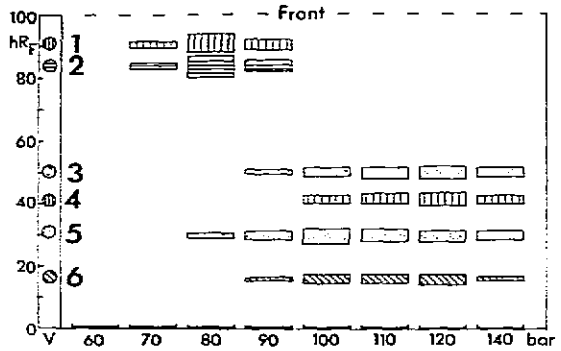

Fig. 10. Thin-layer chromatogram after fluid extraction of fat-soluble dye mixtures at increasing pressures. The amount of flowing carbon dioxide is 1 l in each instance. 1 = Guaiazulene; 2 = azobenzene; 3 = Ceres red; 4 = Ceres blue; 5 = Sudan red; 6 = indophenol.

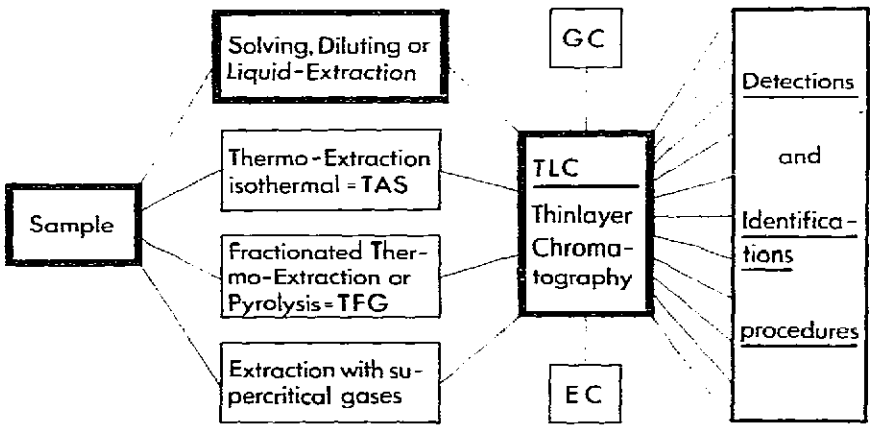

Fig. 11. Summary of the various possibilities of transferring substances from sample to thin-layer starting point.

8. OUTLOOK FOR THE THIRD DECADE

In considering the possibilities for the future, it must be borne in mind that TLC itself is a coupling procedure and consists of three parts (Fig. 12). The question now arises of the part of the procedure in which further progress is still possible and what are the aims. One can assume that a molecule A can be separated from a molecule B by TLC. This separation is, however, not visible. The lower limit of detection by the human eye cannot be significantly improved by either further diminishing the starting

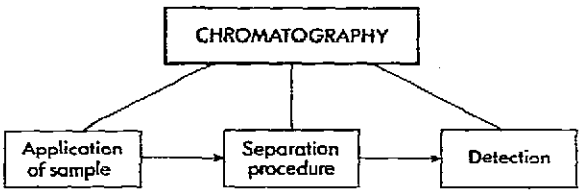

Fig. 12. Illustration that chromatography itself is a coupling procedure and consists of three main parts.

points, by shortening the run or by reducing the grain size of the layer material. Starting points of less than 1 mm and the nanolitre capillaries needed for them are widely considered to be no longer convenient. A much more important objection is, however, the fact that when the amount spotted is reduced to the utmost limit, the subsidiary and trace components usually present in the mixture can no longer be detected. One thus subjects oneself to a deception. It is similar to the use of an insensitive detector in gas chromatography or an insensitive reagent for detection in TLC (Fig. 13). In this way in the microgram range seemingly small zones create the impression of sharp and hence of good separations. The equipment for sample application is sometimes complicated and expensive and further development in the direction of simplification and cost saving would appear desirable. Something new in the sphere of sample application in TLC is, in my opinion, no longer to be expected.

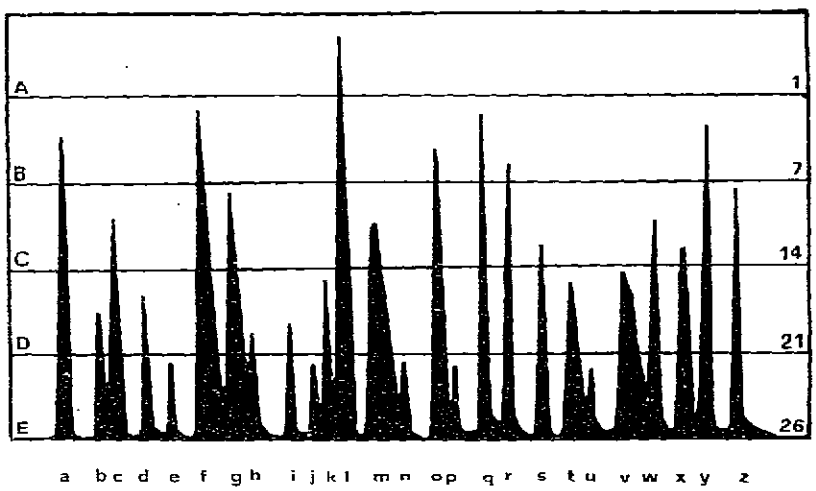

Fig. 13. Peak mountain of 26 substances, arising in various amounts on the chromatogram. In level A the detection is carried out with an insensitive agent, in level B a somewhat better agent allows the identification of 7 components, in level C a sensitive agent identifies 14 components, in level D a still more sensitive agent identifies 21 components and in level E 26 components are identified with a highly sensitive agent. In this range, however, there is a poor separation on account of the overlapping of substances. For a comparison, see the "mock" success of separation in level C.

Genuine progress does seem still possible in the separation systems. This does not mean through an increase or decrease in the plate size or layer thickness but rather through the adsorbents. The possibilities here are not yet exhausted. One should remember how long it took before a definite silica gel product with a narrow range of grain size could be prepared on the technical scale (see Introduction). The best products in this field are used for the industrial preparation of ready-made TLC plates but are still not available to those wishing to prepare layers themselves.

The really high-quality products are often obtainable only as highly expensive small packages for GC or HPLC. Exhaustive scientific investigation and exploration of methods of technical preparation in the vast field of possible adsorbents other than silica gel are also pressing needs. A limit to the solvents used has so far been self-

imposed and materials, other than the usual laboratory solvents and their mixtures have hardly been tried. Many new solvents have become commercially available in the last few years and ought to be tested for their value in solving special separation problems. The properties of a solvent are not determined alone by its dielectric constant.

A broad field, largely unexplored in TLC practice, is that of the gradient techniques. More attention should be paid to these possibilities in future. It is a pity that the relevant manufacturers are content merely to prepare single-stage gradient layers (inactive–active). Gradient layers and gradient elution are as much as ever procedures of future value.

In my opinion, the real emphasis of further development of TLC in the third decade will fall on the detectors (possibilities of detection). The present marked superiority of TLC in detection should be systematically extended. This is relatively easy if one takes into account the tasks and aims of the various organic and biochemical working groups. First, one must be clear that there are necessarily three different "types of detector" (detections):

(1) *Universal detectors:* detection of all compounds.

(2) *Detectors of specific groups:* detection of compounds containing particular functional groups or definite physical or biological properties.

(3) *Detectors of individual substances:* specific detection of individual compounds of a mixture.

A glance at the reagents hitherto used shows that much basic research is necessary here. The development of new biological and pharmacological microdetectors in combination or by coupling with TLC is an attractive and promising field. Another promising and plausible prospect appears to be the development of further specific detection methods for individual substances through suitable fermentation reactions (for example, in clinical diagnosis).

Yet another detection theme is the development of still more sensitive reagents. The conversion of colourless into strongly fluorescing compounds has already provided a good basis for this. One thinks, for example, of the introduction of the fluorescamine reagent in the extremely sensitive fluorescence detection of primary and secondary amines. "Multiplier" reactions, taking place in a similar manner to the sense of the Sandell–Kolthoff reaction, are also conceivable.

Another problem which could be better solved is the completely uniform application of the reagents to the layer, avoiding drops. Promising indications here are from the so-called application via the gas phase. Systematic further study is necessary. The influence of temperature and duration of heating on the optimal development of colour reactions on the thin layer is another study that has been neglected so far. UV lamps of better performance and simpler and cheaper means of documentation of the chromatograms in true colours are also widely desired.

A final question concerns the future of TLC in relation to the other chromatographic procedures. For the following reasons TLC will still remain the most used separation procedure:

(1) the greatest freedom of simple choice of stationary and mobile phases;

(2) the largest number of possibilities of detection (over 250 colour reagents);

(3) the possibility of simultaneous separation and detection of 15 or more samples and reference mixtures on a 20 × 20 cm layer;

(4) the possibility of simple coupling with micro-extraction and identification procedures;

(5) the simplest and cheapest chromatographic procedure for fast qualitative and semi-quantitative separation.

These five advantages justify the statement that TLC will keep its place in laboratories and will develop further. However, despite all possible progress, it must always be remembered that TLC is only one of the possibilities in the domain of separation methods and that research problems are best solved only by the purposeful use of all analytical methods.

9. SUMMARY

In a retrospect of my work on thin-layer chromatography, a summary of results and progress is given. Between 1957 and 1967, emphasis lay on the standardisation of the method, on increasing the number of applications in the hydrophilic field and on the extension of the method to the nanogram range. In the second decade, we developed methods for solvent-free extraction of micro amounts in direct combination with thin-layer chromatography, such as the TAS-procedure, thermofractography and the micro-extraction with supercritical gases.

Finally, the report describes the prospects for the third decade of thin-layer chromatography and the aim of even greater improvement in matters of detection.

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