FRIEDLIEB RUNGE AND HIS CAPILLARY DESIGNS

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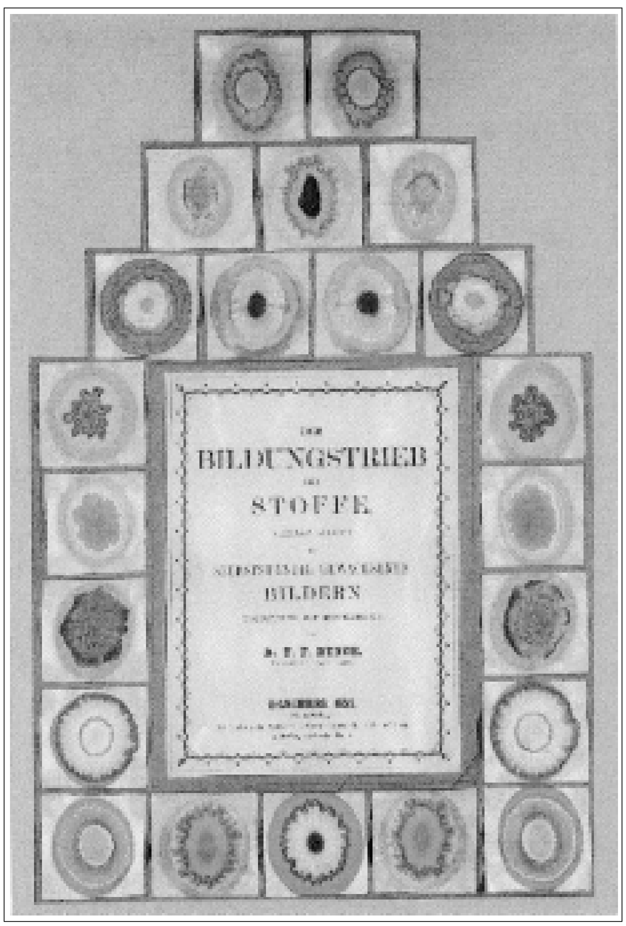
The chemical sciences in modern times owe no small debt to the development of improvements in analytical techniques. Chromatographic methods, in particular, have served as successful, systematic separations in chemistry, biology, and biochemistry. The founder of chromatography is recognized as the Russian botanist M. S. Tswett (1), who in 1906 applied the concept of "chromatography" for the first time. In 1941 the work of British chemists A. J. P. Martin and R. L. M. Synge (2) became world renowned; they were awarded the Noble Prize in 1952 for the development of partition chromatography.



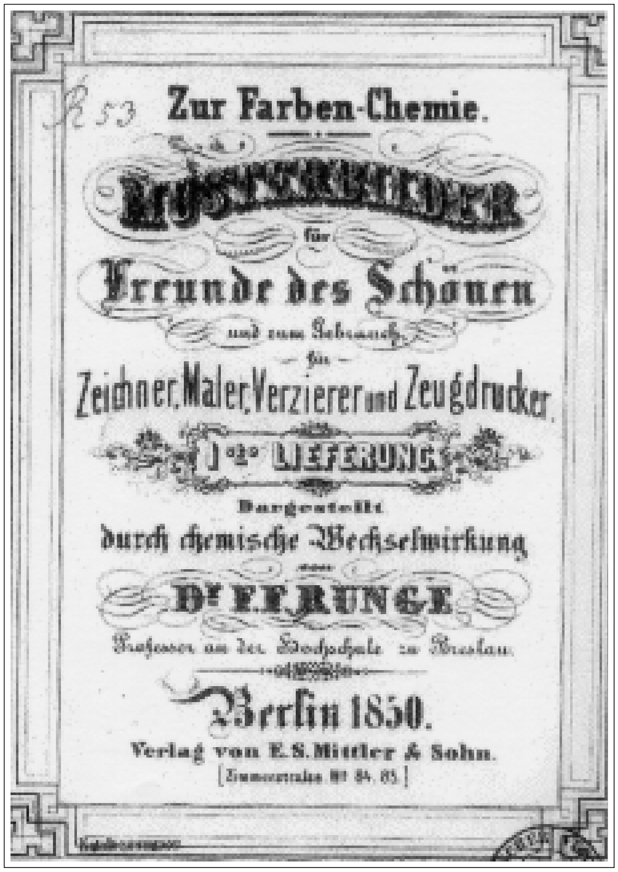
Title page, Der Bildungstrieb der Stoffe, *Oranienburg, 1855.*

By contrast the work of the German chemist F. F. Runge (1794-1867) has remained virtually unknown. About 100 years before Martin and Synge, he took advantage of the capillary action of blotting paper as a means of visualizing chemical changes. In his 1855 book, *Bildungstrieb der Stoffe*, Runge described techniques that are the forerunners of modern paper chromatography.

Who was Friedlieb Ferdinand Runge?

The academic and industrial chemist F. F. Runge was born on February 8, 1794 in Billwerder near Hamburg. After completing an apprenticeship in pharmacy in Lübeck, he first studied medicine in Berlin and then moved to the university in Jena, where he concentrated on plant chemistry. In 1822 he completed his doctoral studies on toxic plant extracts, under the direction of W. Döbereiner (3). He became Professor of Technical Chemistry at the University of Breslau (currently

Wrozlaw, Poland) (4) in 1828.



Title page, Musterbilder für *Freunde des* Schönen, *Berlin, 1850.*

Because he found the meager salary of a professor disappointing, Runge took a position in 1833 at the *Chemische Produktenfabrik* in Oranienburg (5), where he sought the opportunity to bring his creativity and inventiveness to fruition. As technical director, Runge had as one of his assignments finding uses for coal tar oil, a byproduct in the manufacture of illuminating gas (6). In the process he discovered and identified phenol and aniline (7). Much to his surprise, he was able to isolate deep-red crystals from the distillation residue. This *Rosolsäure* yielded a brilliant red dyestuff, the first synthetic textile colorant, suitable for dyeing calico and silk fabrics. Further investigations led Runge to the preparation of violet and bluedyestuffs. When cotton fibers were impregnated with aniline and then treated with copper salts and potassium chromate, there appeared a light-fast black, which could be reduced with sulfurous acid to an emerald green.

Runge informed his supervisors of his discoveries and proposed building a factory in Oranienburg for the manufacture of synthetic dyes and other coal tar products. This took place in 1836, indeed 20 years before the discovery of mauve (8) by W. Perkin (1856). His plan fell on deaf ears at general management in Berlin. He turned to experimenting with stearin and paraffin (9) for the manufacture of candles for domestic illumination, but his proposal to build a candle factory was also denied. Finally, Runge made the suggestion to manufacture "synthetic guano" from bones and other slaughter house wastes for use in agriculture (10). His thought was that the deteriorating fertility of farmland would afford an opportunity for a thriving enterprise and high profits. Once again, however, his message went nowhere.

Runge was bitterly disappointed over the denial of his proposals and the continual disagreements with higher authorities. He accused the ministerial offices of scientific ignorance. In response the executive officers faulted Runge for spending too little time in the factory. In fact, Runge wrote no fewer than seven textbooks (11) during his employment, between 1834 and

Table. Examples of "Runge Designs"

Solution A	"Instrusion Agent"	Solution B	Result
Pb(III) sulfate	—	K ferrocyanide	deep-blue ring with brown border
Mn sulfate	ammonia	K chromate	dark brown ring with light brown border
Cu sulfate	$(NH_4)H_2PO_4$	K ferrocyanide	red core with green border

1850. The conflict ended in 1851 with his dismissal. As a pension Runge received 400 Taler (12) annually and wood to heat his living quarters. In return, he was required to reside in Oranienburg, "so that one could seek his professional advice at any time."

Capillary Designs "for Friends of Beauty"

At the age of 56 Runge could now turn his attention to a hobby that had long fascinated him: color reactions for identifying single components in mixtures. The kitchen of his bachelors' quarters was converted into a makeshift laboratory, with cups and plates serving as substitutes for glass apparatus. He was able to carry out distillations and concentrations with his coal stove. Having been barred from his former work place, he found it necessary to be very sparing in use of chemicals. In this way he became adept at working with very small quantities of material: this was analysis on a microscale. Not wanting to spend his time cleaning test tubes, Runge came upon the idea of carrying out chemical reactions on the surface of blotting paper. Thus he developed a new field of practical chemistry: capillary analysis.

Runge's technique was conceptually simple: a wooden frame (roughly 12 x 12 cm.) was wrapped with cord on which was placed a piece of unsized, adsorbent paper (*Löschpapier*) (13). He introduced a solution of A dropwise by means of a pipet in the center of the paper, being certain that each drop was taken up individually by the paper. After the paper had been allowed to dry, he introduced a solution of B on the exact same spot. The result was the formation on the paper of deposits in the form of characteristic rings, bands, or irregular shapes. The final appearance could be varied at will by the use of "intrusion agents" ["Störsubstanzen"], such as ammonia, hydrochloric acid, oxalic acid, or a small amount of sugar, egg white, or gum arabic. The resulting "Runge designs" resembled in shape the ameba, jellyfish, or a wreath.

Runge concluded that the circular images arose:

> ..durch eine neue, bisher unbekannte Kraft, die mit Magnetismus, Elektrizität und Galvanismus nichts gemein habe ("from a new, as yet unrecognized force but different from magnetism, electricity, or galvinism.")

He called this force the "creative drive" (*Bildungstrieb*) of matter. Today we recognize Runge as the first to identify the principle of chromatography, a method for separation and identification of chemical substances in a complex mixture. He did not extend this basic principle to the next logical step-practical analytical applications. After all, in retirement Runge was assigned no scientific projects (14).

Runge's "Picture Patterns" - Rare Curiosities

Runge's enthusiasm for the beautiful "color spots" prompted him to introduce the "spontaneously formed images" to the public. He encouraged Oranienburg school children to assist in preparing the images, and they in turn were thrilled to collaborate with the prominent scholar. Under Runge's guidance, thousands of chromatograms were produced and, together with scientific explanations, used to embellish books, which were printed privately in limited editions between 1850 and 1855 (15). What has become of these books? About 20 of these rarities can be found presently in various libraries, among them:

- Philadelphia (Chemist's Club Library, Chemical Heritage Foundation)
- Philadelphia (Library of the Philosophical Society)
- Oberlin, OH (Library of Oberlin College)
- New Haven, CT (Yale University Library of Rare Books)

In his last years Runge turned his attention to everyday chemistry. He wrote articles of advice on popular and practical science and its basis in daily work. Tradesmen, for example, learned that lumber could be protected effectively against decay by treatment with coal tar oil. Farmers received advice on the disinfection of cow stalls with bleaching powder (chloride of lime), and pharmacists were instructed on the detection of sugar in urine. Most of the articles were addressed to housewives. They learned why wool stockings should not be laundered in hot water and how rust spots could be removed from white fabrics, namely with oxalic acid. In clear but detailed form, he offered recipes for rapid marinating of meat and preparation of an easily digestible cucumber salad. Runge's articles were later published in book form (16), and he was recognized as the "pioneer of popular chemical formulations."

In Oranienburg Runge was considered an eccentric, cranky independent scholar. In 1862, 28 years after his discovery of coal tar dyes, he was honored with a high tribute at the Industrial Congress in London, and he was finally honored in the Prussian capital of Berlin. He was given honorary membership in chemical societies and received several honorary degrees and awards.

After a short illness, Runge died in his residence in Oranienburg on March 25, 1867, where he was buried in the municipal cemetery.

Conclusion

F. F. Runge, one of the first industrial chemists, discovered and isolated the plant alkaloids quinine, atropine, catechol, and caffeine. From coal tar oil he was able to isolate phenol, aniline, quinoline, and thymol. He was far ahead of his time, having proposed large-scale production of coal tar dyes, wax candles, and synthetic fertilizer. Had he not been impeded but rather encouraged by the Prussian bureaucracy, he might today be considered the founder of pharmaceutical chemistry and coal tar dyes and fertilizer industries. From his publications, Runge can be considered the discoverer of capillary analysis, developed as an analytical tool 100 years later in the form of paper chromatography.

Runge's residence and place of death, Oranienburg

REFERENCES AND NOTES

1. Mikhail Semenovich Tswett (1872-1919), Geneva and Warsaw.
2. Archer John Porter Martin (1910-2002) and Richard Laurence Millington Synge (1914-1994). The separated a mixtures of amino acids from wool hydrolysate on a column of hydrated silica. Nobel Prize in Chemistry, 1952.
3. Johann Wolfgang Döbereiner (1780-1849), known among other things for his lamp and for chemical catalysis.
4. In the cholera epidemic in Breslau in 1831 Runge used bleaching powder for the first time as a disinfectant with great success, thereby earning high respect from the population.
5. The "Chemisches Produktenfabrik" in Oranienburg, north of Berlin, founded in 1802 by the pharmacist G. Hempel, was the most modern chemical factory in Europe at that time. It produced sulfuric acid, hydrochloric acid, soda and in organic pigments. Later a soap factory ("Oranienburger Soda-Seife" was added.
6. The Oranienburg factory used coal gas from coke for thee synthesis of ammonia. This coal gas, supplied by Berliner Gasanstalten, contained residues of coal tar oil, which at the time was of no value.
7. The concept of phenol or aniline was unknown at the time; Runge the substances he discovered as "Carbolsäure (carbo = carbon) and Kyanol (Gr., kyanos = blue).
8. William Perkin (1838-1907) discovered the first coal-tar dye mauve in 1856 and began commercial production in 1857, which ushered in the era of synthetic dyes.
9. Runge obtained stearin from imported palm oil and paraffin from domestic peat. Both raw materials were cheaper than beeswax then being used for candle manufacture.
10. The idea to make "synthetic guano" from slaughter wastes originated with J. von Liebig (1803-1873). The first production of synthetic fertilizer was achieved in Heufeld, Bavaria and Wiesbaden, Hessen in 1857. Runge might have begun manufacture and sale of "synthetic guano" seven years earlier.
11. F. F. Runge, *Farbenchemie*, Teil I., "Die Kunst zu färben," (1834); Teil II., "Die Kunst zu drucken," (1842); Teil III., "Die Kunst der Farbenvorbereitung," (1850), E. S. Mittler, Berlin. F. F. Runge, *Technische Chemie für Jedermann* (1836); F. F. Runge, *Technsiche Chemie der nützlichen Metalle* (1838), Verlag Sander'sche Buchhandlung, Berlin. F. F. Runge, *Grundriss der Chemie*, Teile I und II, Verlag Georg Franz, München, 1846, 1847.
12. The Prussian king later granted him an additional 350 Taler annually, in recognition of his contributions to science.
13. The nature of the paper is crucial for the success of the chromatogram. Thin, unsized, highly absorbent cotton or linen paper is recommended. It must be homogeneous and as flat as possible, such that the capillary designs may freely develop.
14. The "Tüpfelmethode"—spot test—developed by the Austrian chemist Fritz Feigl (1891-1971) was but a short step further. Another Austrian chemist, Fritz Pregl (1869-1930), was awarded the Nobel Prize in Chemistry in 1923 for his development of qualitative and quantitative microanalysis.
15. F. F. Runge, *Farbenchemie. Musterbilder für Freunde des Schönen und zum Gebrauch für Zeichner, Maler, Verzierer und Zeugdrucker, dargestellt durch* chemische Wechselwirkung, Selbstverlag, Berlin, 1850. F. F.

Runge, *Der Bildungstrieb der Stoffe, veranschaulicht in selbstständig gewachsenen Bildern (Fortsetzung der Musterbilder),* Selbstverlag, Oranienburg, 1855.
16. F. F. Runge, Hauswirthschaftliche Briefe," 1-3, Dutzend G. A. Koenigs Verlag, Berlin, 1866, Oranienburg, 1867; reprinted by VCH-Verlag, Leipzig and Weinheim, 1988.

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2. G. Harsch and H. Bussemas, *Bilder, die sich selber malen,* Dumont Verlag, Köln, 1985.
3. M. Rehberg, *F. F. Runge, Entdecker der Teerfarben,* Oranienburg, 1935, publisher unknown; included in: A. Grüne, *Das Chemische Wappen*, zum 100jährigen Gedächtnis von Runges "Bildungstrieb der Stoffe," Schleicher und Schüll, Dassel, 1955.
4. K. A. Schenzinger, *Anilin* (a novel), Zeitgeschichte-Verlag Andermann, Berlin, 1936.
5. E. F. Schwenk, *Sternstunden der frühen Chemie,* Verlag C. H. Beck, München, 1998 and 2000.
6. J. Zahn, "Dr. Gift und die ersten Anilinfarbstoffe," in *Farben-Revue,* Bayer, Ludwigshaven, 1985, 47 ff.

ABOUT THE AUTHOR

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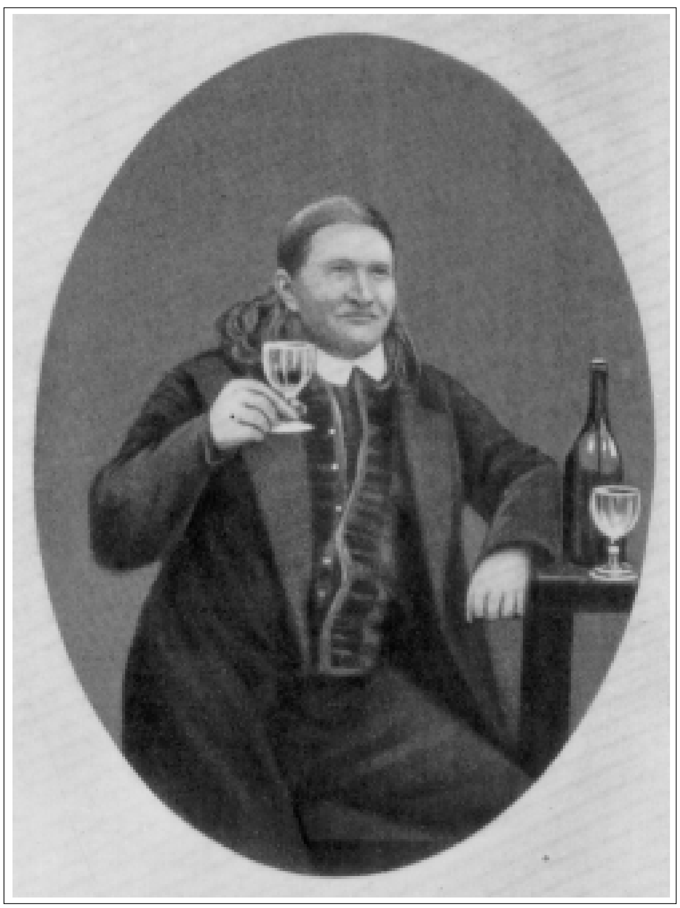

Runge with his home made gooseberry wine (Photograph ca 1860, the only one known to exist.)