

Milestones in Chromatography

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This month's "Milestones in Chromatography" discusses the activities of F.F. Runge, a 19th century scientist whose investigations could be considered a precursor of chromatography.

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Editor

Forerunners of Chromatography: Runge's Self-Grown Pictures

Yale University's Beinecke Rare Book and Manuscript Library has many of the world's rarities. One could be of particular interest to chromatographers. It is a 43 cm \times 26.5 cm book composed of black cardboard pages containing 32 multicolor pictures, each about 12 cm \times 14 cm, and often shown in duplicate to illustrate that they can be reproducibly prepared. At first glance the pictures look like circular chromatograms on paper. They were made individually and glued on the cardboard pages; each has an explanation of how they were prepared. The title page has 22 color pictures around a centerpiece that gives the title of the book (in German), as "The Od as the Driving Force of Formation of Substances, Visualized by Self-Grown Pictures." The author is given as F.F. Runge, professor of technology; it is indicated that he published the book privately and its price is given as four Thaler. The book was published in Oranienburg (today, a suburb of Berlin), in 1866.

Who was Dr. Runge and why do we mention him as a milestone in chromatography? After all, chromatography was invented in 1903 by M.S. Tswett, almost 40 years after Runge's book. Still, due to his "self-grown pictures" Runge's work could be considered as the forerunner of paper chromatography.

Runge's Life and Activities

Although today he is mostly forgotten, Friedlieb Ferdinand Runge counts as one of the important pioneers of medicinal and industrial chemistry of the first part of the 19th century, during the beginning of the industrial revolution. He was born on February 8, 1794, in Billwerder, a small village just southeast of the great German seaport Hamburg, where his father was the town's pastor. When he was 16 years old he went to Lübeck, a town northeast of Hamburg, to start an apprenticeship in the pharmacy of his uncle. After six years, however, he

changed his mind and enrolled in the new University of Berlin (founded in 1809) to study medicine. Two years later, he moved to the famous university in Göttingen and then, within a year, to the University of Jena where he received his medical doctorate in 1819. However, he never practiced medicine. In his last university years he turned more and more toward chemistry and the study of the (particularly poisonous) compounds present in plants. Even his thesis for the M.D. degree was in this field, dealing with the study of atropine, a constituent of the plant belladonna.

At the end of 1819 Runge moved to Berlin, becoming a Privat Dozent (associate professor) in chemistry at the university. In Jena he already started to write a book about the biologically active ingredients of plants; the first volume was published in 1820 and the second in 1821. He also studied the active substances of coffee beans (caffeine) and cinchona bark (quinine); the effect of these two plants had been known for some time, but Runge was the first to discover the existence of their active substances.

In 1822 Runge obtained a Ph.D. degree in chemistry at the University of Berlin, with a thesis on the dye indigo. He presented two lectures: one on the interaction of color and mass of plant materials, and the second on the definition of plant poisons and nutrients. At that time he also started to be interested in technical chemistry, a very new discipline.

In 1823 Runge moved to Breslau (today: Wrocław, Poland) and became associated as a Privat Dozent with the local university. However, after a few months he embarked on a more than two years-long journey through Switzerland, France, the Netherlands, and England as a companion of the son of Carl Milde, a rich factory owner in Breslau, visiting laboratories and studying industrial plants and agricultural installations. After returning to Breslau in 1826, Runge joined the textile factory of Milde,



Figure 1: F.F. Runge in the last years of his life.

where he became familiar with textile dyeing. He also continued teaching at the university, and in 1828, he was appointed an adjunct professor for technical chemistry. Runge also started to write chemistry textbooks; the first was published in 1830, and he continued this activity for more than 15 years. Runge's intention was to teach chemistry to everybody and he apparently was successful in this. The popularity of his chemistry textbooks is best shown by the fact that his last book published in 1846–1847 was printed in 15,000 copies, an enormous number at the time.

In 1832 Runge left Breslau to join the chemical factory of Dr. Hempel in Oranienburg. He remained associated with this factory for 20 years as its technical director. It is, however, interesting to note that in all his publications, even after his association with this factory and in retirement, he continued calling himself a professor of the University of Breslau.

The factory in Oranienburg was one of the very early German chemical factories; it was established in 1814. Its main products were sulfuric acid, potassium ferro- and ferrocyanide, candles, and soap. From these, potassium ferrocyanide ($K_4Fe(CN)_6$) was probably the most important: it was the starting material of the dye Prussian blue. A large part of production was exported. Data for 1845 show that the total production was 162,815 pounds and from this 75,530 pounds were exported, among them 35,500 pounds to New York City. At that time over 150 people worked at the factory (1).

During his long association with the Oranienburg factory Runge contributed

significantly to the improvement of its production methods and the widening of its product line. In addition he also carried out major research, particularly related to coal tar: he was the first to isolate phenol and aniline, prepared by their reaction with other compounds some colored dyes, and also isolated paraffin wax, which he used for the production of candles. Readers who are interested in Runge's activities as an industrial chemist are referred to two relatively recent publications (2,3).

Runge retired from the factory by the end of 1852, but for a few years he continued to serve as a consultant. He devoted his time to his books, to his "chromatography" activities and to some additional experimental work, among others making wine from various fruits. We have one photograph from this period showing Runge with a bottle of his favorite wine (Figure 1). During his retirement he received a pension from the King of Prussia. Runge died on March 25, 1867.

Below we shall discuss in detail Runge's activities that resemble chromatography. Our discussion will be organized according to his major books dealing with such matters.

Investigation of Dyes

Runge's interest in colors was a consequence of his work at Milde's textile factory in Breslau, where he became involved in textile dyeing. He maintained his interest in this field even after moving to Oranienburg where he started to summarize his knowledge in a book series. The first volume of his *Farbenchemie* ("The Chemistry of Coloring") was published in 1834 and it discussed the dyeing of cotton (4); the second volume dealing with textile printing was published eight years later (5); and finally, the third volume handling the preparation of dyes was published in 1850 (6). All three books contain as illustrations small, original pieces of fabric, showing dye patterns. In the third volume he also mentions that a piece of filter paper is very useful to test dye solutions. To quote, "due to its capillary force it separates a drop spotted on it into its components and . . . creates a picture with a dark colored center part and lightly colored or even colorless rings or areas."

Runge was a very practical chemist: if he observed a new phenomenon he immediately explored whether it had any practical use. He became fascinated with the behavior of filter papers separating a simple color into its components and realized that this phenomenon could be used to study the

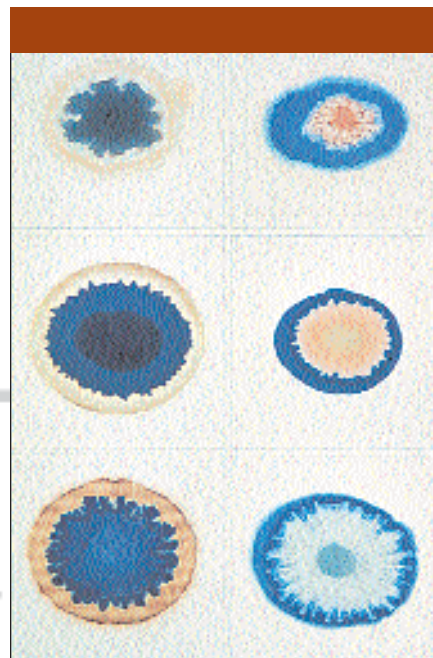


Figure 2: One page of Runge's *Musterbilder*, with pictures 91–96 (1950).

reaction of dark dyes that would have been difficult to follow in solution, because the dark color obscured the changes that took place. On the other hand, on a filter paper strip the components present in the original dark solution were separated, permitting observation.

One of Runge's experiments illustrates his use of filter paper strips for such a purpose. He wanted to quantitate a natural plant dye by precipitating it with the addition of lead acetate solution. However, due to the dark color of the original solution, there was no way to observe or test whether the precipitation was complete. On the other hand, using a filter paper strip, testing was simple. After successively adding lead acetate to the dye solution, he spotted one drop of the supernatant solution on a filter paper strip, and added one drop of a potassium chromate solution next to it. The spots started to diffuse away from the spotting points and eventually met. If the precipitation was not yet complete, there was no lead acetate present in the supernatant solution and thus, nothing happened at the place where the two diffusing rings merged. On the other hand, if the precipitation was complete and there was an excess lead acetate in the supernatant solution, its reaction with potassium chromate (forming lead chromate) on the filter paper resulted in a dark yellow color. In this way the completeness of the dye precipitation could be easily followed.

The Formation of Characteristic Patterns

The third volume of Runge's *Farbenchemie* was published in 1850; however, Runge had started to use filter paper strips to follow reactions much earlier. In his later chemistry textbooks he also illustrated chemical reactions in this way: when solutions of two reagents were spotted next to each other, the reaction products formed where the two diffused spots met. Thus, at the beginning of his work in this field, he definitely had practical uses of such investigations. However, slowly he became more and more fascinated by the obtained pictures and started to "play" with the various possibilities, using a variety of reagents just to see what happened if they interacted on the filter paper strips, forming various multicolor patterns.

Evidently by 1850 Runge collected a large number of such patterns and, simultaneously with the third volume of his *Farbenchemie*, published a collection of these pictures (7). He announced its publication at the end of the third volume of his *Farbenchemie*, mentioning that he just published a book "about similar pictures that are of importance for the *Farbenkünstler* [color artist], and particularly for the pattern maker." It is a fairly large, 26 cm \times 19.5 cm, hardcover book with a very long title the English translation of which is "To Color Chemistry. Pattern Pictures for the

Friends of Beauty and for Use of Draftsmen, Painters, Decorators and Textile Printers, Prepared by Chemical Reactions." In the literature this book is usually referred to by the main word of the German title as *Musterbilder*. It was dedicated to King Frederick William IV and Runge presented a copy to him; the king answered in a handwritten note, stating that he enjoyed it very much.

A six-page long introduction explained the purpose of the book: to show that by mixing various substances on a filter paper strip, very special, multicolor pictures are obtained during the spreading of the spots. These pictures are highly specific of the starting substances and their mixing ratio, and even the sequence of spotting. They also are highly reproducible. In Runge's opinion these pictures illustrated the reactions during mixing and separation of the various components much better than any experiment a teacher could carry out during a lecture. As he stated, "one can write a chemistry textbook with the help of these pictures and explain everything much easier." According to Runge such pictures have a further advantage as compared with laboratory demonstration experiments: they are like a map, recording the whole reaction process, not just the end product of the reaction.

This introduction is followed by 21 pages, each containing six 4 cm \times 5 cm pictures. Each was individually handmade (quite a job), by first spotting the solution of a substance (or substance mixture) on the paper and then, after drying, adding a drop of the next reagent or reagent mixture. Various inorganic salts were used as the reagents such as chromium, copper, iron, manganese, or sodium sulfate, ammonium dihydrogen phosphate and potassium ferro- or ferricyanide. As an illustration Figure 2 shows the page containing pictures 91–96.

As mentioned previously, Runge originally started these investigations to be able to study reactions more easily. In this respect one can consider his work as the start of paper chromatography. After all, he carried out reactions on filter paper strips and followed them by separating the reagents and reaction products. However, soon the practical use of this process was replaced by an artistic, almost philosophical description of the pictures. In subsequent years Runge moved even more toward an almost mythical interpretation of his pictures. This becomes clear in his next book published five years later,

representing a further collection of his pictures.

Self-grown Pictures

The title of Runge's new book, published in 1855 (8), indicates this change in his interpretation of the pictures obtained by mixing reagents on a filter paper strip. The translation of the book's title is "The Driving Force of Formation of Substances, Visualized by Self-Grown Pictures" and it is indicated as a continuation of the *Musterbilder*, his previous book. In the literature this book usually is called the *Bildungstrieb*, after the second word of its German title. It looks more like a large notebook, comprising 43 cm \times 26.5 cm black cardboard pages, with a total of 32 original pictures, each about 14 cm \times 12 cm, glued onto the cardboard pages. Most of the pictures are given in duplicate to show how reproducibly they can be prepared. The book has an outside and an inside title page. The inside title page has a centerpiece giving the title and other information, which is surrounded by 22 color pictures (Figure 3). The outside title page is an enlarged copy of the inside centerpiece, without the surrounding pictures.

In the book a printed text was given next to each figure, listing the reagents and their proportions used in creating the picture. In addition this text also presents some explanation of the reagent choice and

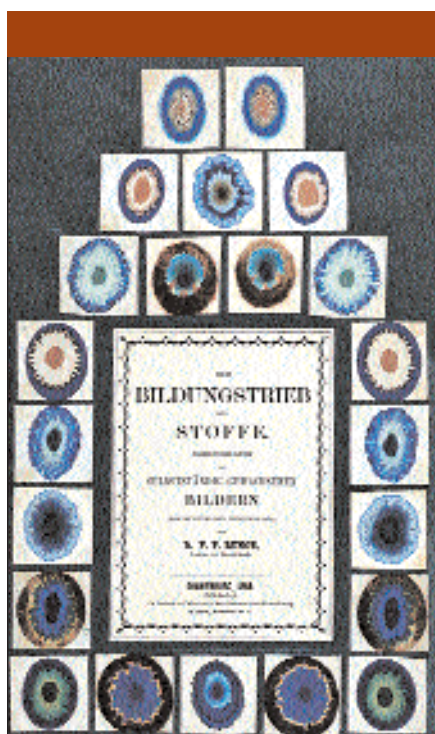


Figure 3: The title page of Runge's *Bildungstrieb der Stoffe* (1855).

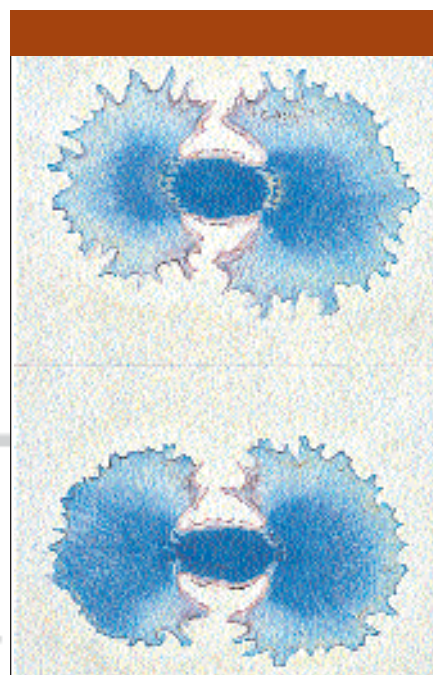


Figure 4: Picture 24 in Runge's *Bildungstrieb*. Solutions of the following reagents were used: MnSO_4 , Na_2SO_4 , $(\text{NH}_4)_2\text{H}_2\text{PO}_4$, $\text{K}_3\text{Fe}(\text{CN})_6$, and AlCl_3 .

often gives a poetic description of the figure. As an example, the text accompanying Runge's picture 24 (Figure 4) is given here:

Everybody who sees these horror pictures will automatically ask, "can the driving force also create monsters?" These pictures are certainly not well formed, but are peculiar enough to merit a place here. When somebody sees such a picture, he will most likely believe that it is the result of an accident. However, when he sees two or — like me — thousands of identical pictures, then he must start to realize the presence of a legality, expressed by both the outside and inside formation force.

As a further illustration of Runge's wide variety of pictures included in *Bildungstrieb*, three more are given here as examples (Figures 5–7).

It is worth mentioning that each picture in both books (the *Musterbilder*, as well as the *Bildungstrieb*) was prepared individually for each copy, and was then glued to the proper place. Even although the books have been published in limited editions, Runge had to prepare (we might even say, produce) hundreds, if not thousands, of pictures. At the end of the *Bildungstrieb*, Runge explains how the pictures were prepared: he actually engaged children to carry out the work, by spotting the reagent solutions (prepared by himself) on precut paper strips, using specially designed tools.

We should mention here that despite of the unusual (we might say, unscientific) explanations, the *Bildungstrieb* was well received by Runge's peers: he received for it the special medal of the World Exhibition held in 1855 in Paris, and the book also was honored by the World Industrial Exhibition held in 1862 in London. Thus, the scientific world knew about Runge's work and considered it worth for recognition.

The Driving Force of Formation

We should deal briefly with the concept of the "driving force of formation" (*Bildungstrieb*) indicated in Runge's book. He believed in the existence of it as a special force of nature. Actually this expression was not his invention: it originated from J.F. Blumenbach (1752–1849), professor at the University of Göttingen where Runge studied. Blumenbach postulated that a special force exists within living organisms and this is responsible for production, reproduction, and nutrition; he called this

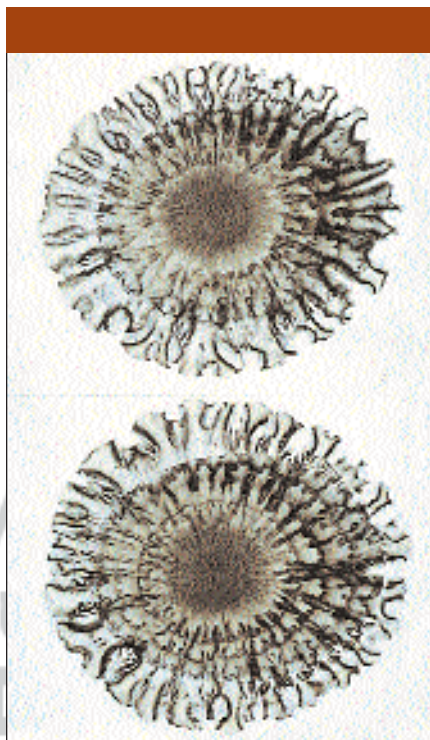


Figure 5: Picture 10 in Runge's *Bildungstrieb*. Solutions of the following reagents were used: MnSO_4 , Na_2SO_4 , K_2CrO_4 , and NH_4OH .

the "driving force of formation." Runge came to believe that color formation also represents a new natural force, another "driving force." He explained this in his book in the following way:

I believe . . . that in the formation of

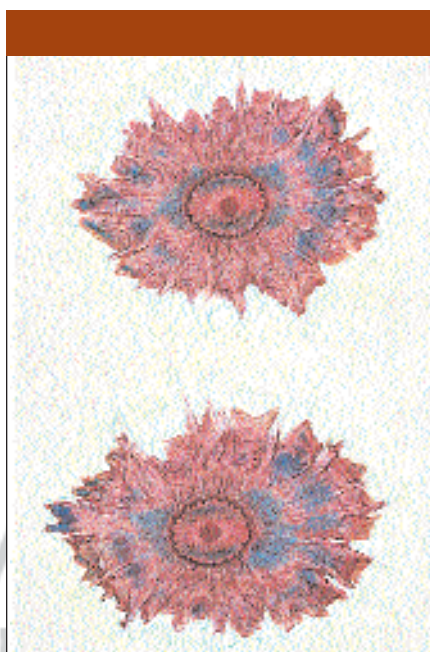


Figure 6: Picture 22 in Runge's *Bildungstrieb*. Solutions of the following reagents were used: MnSO_4 , CuSO_4 , $(\text{NH}_4)_2\text{H}_2\text{PO}_4$, $\text{K}_3\text{Fe}(\text{CN})_6$, and KOH .

these pictures a new, until now unknown, force is active. It is excited or attacked from the outside, but it is living within the substances and becomes active when the interactions equalize in their chemical opposition; that means it binds and separates through attraction and repulsion . . . I consider (this force) as a sign of the vitality working in plants and animals.

It is interesting to compare Runge's belief with the philosophy of Johann Wolfgang von Goethe (1749–1832), the great German writer, philosopher, and statesman. Runge met Goethe during his student time in 1818–1819 in Jena, and admired the great man. Goethe also was fascinated by the multitude of colors and spent decades investigating their interactions. As a compilation of his thinking, Goethe published in 1810 a book entitled *Farbenlehre* ("The Science of Colors") and in it, he expressed his belief that colors have a meaning on their own; they show "a distribution, a unification, an antithesis, an indifference . . . in a high, multiple, decisive, instructive and promoting meaning" (8). This is not very far from Runge's own thinking.

The Od

We cannot finish the discussion of Runge's work without mentioning this odd philosophical term and Runge's usage of it. It originated from Karl von Reichenbach (1788–1869), one of the important chemists of the early 19th century. When studying different physicochemical and psychophysiological phenomena Reichenbach introduced the idea of "the Od." Under this term he meant "a hypothetical force to pervade all nature," that can be considered as the basis of almost everything; it might even be present in certain human beings and it can be radiated from the fingertips of such persons! Reichenbach published on this concept in 1845 in the prestigious German journal *Annalen der Chemie*. Although his theory slowly was disregarded, the term crept into the English language and remained there. Most likely our readers have never heard about it and therefore, they will be surprised to realize that it is still included in modern dictionaries such as the *Oxford Dictionary of the English Language* (we checked its 1961 edition [10]), and even in our good old *Webster's*: according to its 1976 edition the Od is "a hypothesized force in nature, formerly thought to manifest itself in such phenomena as hypnotism, magnetism,

light, etc.” (11).

Reichenbach's philosophy about this special force was not very far from Runge's hypothesis about the “driving force of formation,” and therefore, it should not be surprising that eventually, he combined it with Reichenbach's “Od.” This is demonstrated by a very peculiar book, the one in the Rare Books Library of Yale University mentioned in the introduction. This book is almost identical to the *Bildungstrieb*, except that it has a different centerpiece on its title page (Figure 8). A close investigation of the book shows that the new centerpiece was actually glued over the original. Instead of the original text of “The driving force of formation . . .” it now said “The Od as the driving force of formation . . .” There is no further information available about this book and it is not mentioned in earlier Runge biographies such as the book of Rehberg (1). According to our best knowledge the book in the Yale Library is the only existing copy.

We should mention that Runge's other “chromatography” books also are great rarities. Only about a dozen copies exist of the *Musterbilder* in European and American libraries, and even fewer copies of the *Bildungstrieb*.

Runge as a Precursor of Chromatography

Runge's “self-grown pictures” certainly look like circular paper chromatograms and some scientists even accepted his priority in the discovery of paper chromatography (12). At the same time, others considered his work only “one of the most original scientific playing” (13), or “playing with colors and forms” (14). It is very difficult to make an objective judgment on this question.

As mentioned, at the beginning Runge used his pictures on filter paper strips in a true analytical sense. The application to follow chemical reactions by separating the various reaction products as rings or spots of different colors is certainly not far from the meaning of chromatography. Thus, in this respect it is not incorrect to consider his work as a precursor of chromatography. On the other hand, his “self-grown pictures” had no analytical purpose anymore: their aim was simply to create complex, multicolor pictures that please the eye. Also, certainly, his invocation of a special force of nature has nothing to do with chromatography; in fact, it has nothing to do with science.

Still, the overall conclusion is positive.

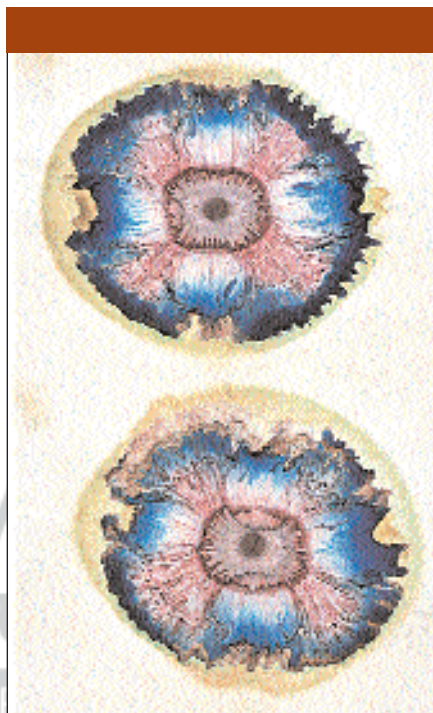


Figure 7: Picture 30 in Runge's *Bildungstrieb*. Solutions of the following reagents were used: CuSO_4 , FeCl_3 , $(\text{NH}_4)_2\text{H}_2\text{PO}_4$, and $\text{K}_4\text{Fe}(\text{CN})_6$.

Runge certainly was the first scientist who demonstrated the possibility of using filter paper strips as a medium to follow reactions and the first to draw attention to the role of separation in such investigations. Thus, even if it would be unjustified to call him the originator or the inventor of paper chromatography, we can still consider him as one of the scientists who showed the way that eventually led to chromatography.

Acknowledgement

Some of the material in this article origi-

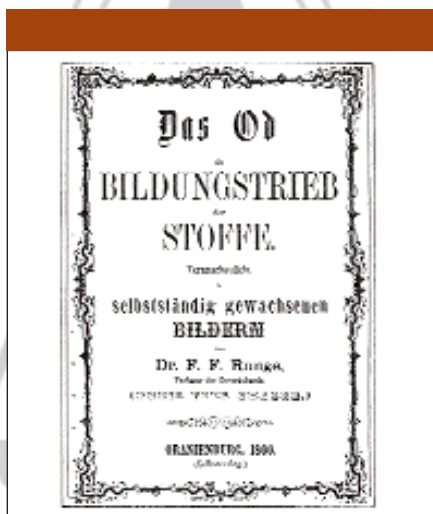


Figure 8: Centerpiece of the title page of Runge's book *Das Od als Bildungstrieb der Stoffe*.

nally appeared in our article published in 1994 in *Chromatographia* (3). The figures are from the collection of one of us (HHB).

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