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EXPERIENTIA MAIORUM

The Origin of Column Chromatography

Layering effects resulting from the percolation of solutions through columns of finely divided materials have been observed since the time of ARISTOTLE, arising during such processes as water purification and dyeing. The date at which the phenomenon was first applied for chemical analysis is not easily defined but is certainly very much earlier than is generally supposed.

MATTEUCCI¹ described the use of a column for the analysis of solutes in organic solvents; the book in which the description occurs was published in English translation in 1847. This translation was known to WAY, an English soil chemist who in 1850 and succeeding years published² accounts of experiments resulting in spatial separations on columns by methods not materially differing from those used by TSWETT in 1903³. It was, incidentally, also in 1850 that RUNGE⁴ described the first paper chromatograms. WAY's experiments were based on research previously carried out by THOMPSON, HUXTABLE, LIEBIG, and others on such problems as the purification of liquid manure and the fixation of ammonia by soils; he used tall narrow columns filled with soil through which solutions were forced under pressure. The separation of zones was achieved either mechanically, by extruding and slicing the column as TSWETT did half a century later, or by forming what is now known as a liquid chromatogram. Separation was improved by washing the columns with distilled water and he thus anticipated TSWETT's process of development. He noted the exchanges which can occur on such columns and thus unwittingly practised what we now call ion-exchange chromatography.

These spatial separations observed by WAY – effected also by other soil chemists of the day – were, however, only incidental to his main aim, the separation of soil solutions into two parts, a filtrate and an adsorbate. The failure of WAY and his contemporaries to exploit the analytical possibilities of this discovery probably derived also in part from an erroneous belief that irregularities of flow, sufficient to make the separations no more than semi-quantitative, were unavoidable.

¹ C. MATTEUCCI, *Lectures on the Physical Phenomena of Living Beings* (London, 1847).

² J. T. WAY, *On the power of soils to absorb manure I*, J. roy. Agric. Soc. England 11, 313 (1850); *On the power of soils to absorb manure*, *ibid.* 13, 123 (1852); *On the use of town sewage as manure*, *ibid.* 15, 135 (1854).

³ M. TSWETT, *A new category of adsorption phenomena and their application in biochemical analysis*, Proc. Warsaw Soc. nat. Chemists (Biology Section) 14, Minute No. 6; *Physikalisch-chemische Studien über das Chlorophyll. Die Adsorptionen*, Ber. dtsh. bot. Ges. 24, 316 (1906); *Adsorptionsanalyse und chromatographische Methode. Anwendung auf die Chemie des Chlorophylls*, *ibid.* 384. – See also: H. WEIL and T. I. WILLIAMS, *M. TSWETT's First Chromatographic paper, to be published* (a translation of 3a in English and an introduction thereto).

⁴ F. F. RUNGE, *Farbenchemie*, III (Berlin, 1850). – *Zur Farbenchemie, Musterbilder für Freunde des Schönen und zum Gebrauch für Zeichner, Maler, Versierer und Zeugdrucker* (Berlin, 1850). – See also: H. WEIL and T. I. WILLIAMS, *Early history of chromatography*, Nature 167, 906 (1951); *Der Ursprung der Papierchromatographie*, Naturwissenschaften (in the press).

Although WAY's experiments unquestionably resulted in the formation of column chromatograms¹, his failure to exploit their analytical possibilities does not invalidate the claims of DAY, in 1900, and of ENGLER, in 1901, to have been the first practitioners of column chromatography for analysis². DAY and ENGLER, and subsequently TSWETT, systematically exploited for analytical purposes the layering phenomena which occur on columns. Both DAY and TSWETT were most probably familiar with WAY's publications. They would certainly come within DAY's field of interest as a geologist, and TSWETT in his very first chromatographic paper³ deals specifically with adsorption phenomena in soils.

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Zusammenfassung

Säulenchromatographie wurde schon lange vor den von TSWETT im Jahre 1903 angestellten Versuchen verwendet, die, wie allgemein angenommen wird, das Verfahren erstmalig eingeführt haben. J. T. WAY hat schon ein halbes Jahrhundert früher ähnliche Trennungen durchgeführt, wenn auch zu einem andern Zweck und wahrscheinlich durch noch frühere Versuche von MATTEUCCI angeregt; DAY und ENGLER haben 1900 bzw. 1901 Analysen von Petroleum mittels der Säulenchromatographie ausgeführt.

¹ T. I. WILLIAMS and H. WEIL, *The definition of chromatography*, Nature (to be published).

² H. WEIL and T. I. WILLIAMS, *History of chromatography*, Nature 166, 1000 (1950); *The phases of chromatography*, Arkiv Kemi, Mineralogi och Geologi (in the press).

³ M. TSWETT, *A new category of adsorption phenomena and their application in biochemical analysis*, Proc. Warsaw Soc. nat. Chemists (Biology Section) 14, Minute No. 6; *Physikalisch-chemische Studien über das Chlorophyll. Die Adsorptionen*, Ber. dtsh. bot. Ges. 24, 316 (1906); *Adsorptionsanalyse und chromatographische Methode. Anwendung auf die Chemie des Chlorophylls*, *ibid.*, 384. – See also: H. WEIL and T. I. WILLIAMS, *M. TSWETT's First Chromatographic paper, to be published* (a translation of 3a in English and an introduction thereto).

100 Jahre solarerterrestrische Erscheinungen

Zur Entdeckung der 11 $\frac{1}{3}$ -jährigen Periode der Sonnenfleckentätigkeit durch RUDOLF WOLF (1852)

Der Spott des grossen Enzyklopädisten der Astronomie, J. J. LALANDE¹, über die Sonnenforscher, die sich mit der Beobachtung von Flecken abmühen, welche wegen der Zufälligkeit ihrer Gestaltung doch niemals ein seriöses Objekt der mathematischen Astronomie sein könnten, war noch nicht vergessen, als der Begründer der Sternwarte der ETH. in Zürich (damals noch Professor in Bern) 1852 zum ersten Male in einer umfassenden Studie nicht nur eine exakte Periode für die Sonnenfleckentätigkeit, sondern auch für die Schwankungen des erdmagnetischen Feldes nachweisen konnte². Frei-

¹ J. J. LALANDE, *Astronomie* (3 éd.) 1791.

² *Neue Untersuchungen über die Periode der Sonnenflecken und ihre Bedeutung*, Berner Mitt. nat. Ges. 1852.