

A Century of Chromatography — Gas Analysis in the First 50 Years

John V. Hinshaw, Serveron Corp., Hillsboro, Oregon, USA.

Although many decades intervened between the beginnings of chromatography as a liquid–solid adsorption technique and the formal invention of gas–liquid-phase chromatography, those years were full of advances in gaseous chemical separations. This month in “GC Connections,” John Hinshaw reviews the developments before 1952 that established the basis for the modern practice of gas chromatography.

The date 21 March 2003 marked the passage of 100 years since Mikhail Tswett (1872–1919) presented a lecture to the Biological Section of the Warsaw Society of Natural Scientists on his 1901–1903 investigations of liquid–solid adsorptive separations of plant pigments at Warsaw University.¹ This lecture is generally recognized as the first public disclosure of the chromatographic technique, although the term *chromatography*, which Tswett coined, did not appear in print until several years later in 1906. Tswett pursued his studies in Russia and Poland and made lecture trips to Germany, France, Belgium and the Netherlands, so his work was not unknown to scientists in Western Europe. Several pioneering researchers in Europe and in the United States extended Tswett's work during his lifetime, but liquid chromatography (LC) separations in general languished until the 1930s, when the scientific world began to understand the significance of LC separation and apply it to various chemical separation and analysis problems.²

At the same time, but largely unknown to those scientists involved with Tswett's work, different researchers investigated gas adsorption on solid substances, which was important to mining and associated businesses at the start of the twentieth century. Certainly, there was little prospect for anyone of that time to make the connection, which is so familiar to

twenty-first century separation scientists, between gas- and liquid-based chromatography separations; they worked in entirely different disciplines with divergent goals. Not until the 1940s did some begin to draw the analogy between their work with gaseous separations and separations with a liquid mobile phase. Yet, various separation techniques based upon gas adsorption, which scientists now consider to have been forms of chromatography, gained significance in the expanding petroleum industry and related chemical endeavours of the 1920s and 1930s.

Separations based upon gas–solid adsorption and desorption preceded gas–liquid partition chromatography by decades, although much of the equipment used before the 1940s might be unrecognizable to modern gas chromatographers. However, these precedents had already established much of the theoretical and practical basis for gas–liquid partition chromatography by the time that A.T. James and A.J.P. Martin began their experimental work with liquid-coated stationary supports in 1950 at the National Institute for Medical Research (London, UK). Two recent publications by L.S. Ettre^{3,4} describe the evolution of gas adsorption chromatography until 1952 in more detail than is possible to include here. I am indebted to Ettre for much of the information that appears in this “GC Connections” column.

Gas Adsorption

Modern chromatographers are familiar with gas chromatography (GC) column packings that are the direct descendants of charcoal. These packings include Carbo-pack-B (Supelco-Sigma-Aldrich, Bellefonte, Pennsylvania, USA), which contains a surface area of 100 m² — roughly equal to the area of my laboratory floor — in 1 g. Adsorption is the primary physical effect used in the various gas separation techniques discussed in this column, including gas–solid chromatography (see the accompanying sidebar “How Do Adsorption and Absorption Differ?”). Adsorption, however, occurs in gas–liquid partition chromatography when solute molecules dissolve into the stationary liquid phase. Gas–liquid partition chromatography can encompass adsorption in addition to absorption when an adsorptive support is coated with a liquid phase to generate a specific mixed-separation effect. Today, adsorptive separations constitute a small fraction of GC methods, although they play a very important role in the chemical and petroleum industries.

The strong adsorption of gaseous components such as hydrogen, methane, ethane, propane and higher hydrocarbons, carbon dioxide and sulphur dioxide onto charcoal was well known at the beginning of the previous century: miners who noted that charcoal would sweeten mine gas

might have discovered it. Scientists of the time began to incorporate adsorption–desorption phenomena into chemical processing and analysis, activities that formed the basis for many modern processing techniques.

Permanent gas adsorption onto charcoal is fine if the objective is air purification, but when testing gas mixtures and the chemical processing of larger quantities of materials is the goal, researchers need a way to recover them from the adsorbent bed. Today, chromatographers classify the possibilities for desorption from an organized adsorbent bed into three broad categories: displacement, frontal development and elution. Strictly speaking each of these categories constitutes a form of chromatography. This commonality was not formalized, however, until many years later.

In the first part of the twentieth century, the displacement of weakly adsorbed gases with a strongly adsorbed substance was the primary means for recovering gases from the sorbent beds used in the chemical and natural gas industries. Frontal development, in which the sample itself served as a displacer, was also known, but it is better for selective purification than for analysis because it results in a gas mixture exiting the bed. Frontal development won't be discussed further in this column.

In elution, a carrier gas conducts substances along a sorbent bed, but the amount of each substance is limited because users can place only a small portion of a mixture at the beginning of the adsorbent bed. Elution was used

primarily for analytical problems only later in the development of gas chromatography. Today, elution is the way in which practically all chromatographic separations are performed. With these categories in mind, I'll provide a brief overview of the major developments in gas chromatography before 1952.

Displacement

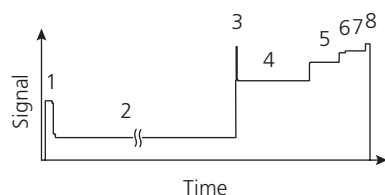
In the displacement development technique, an adsorbent-filled tube is charged with a known gas sample volume, usually enough so that nearly the entire bed is saturated with each gas in the mixture. Then a displacer substance — glycerol, mercury vapour or any of various heavy organic vapours — is introduced gradually into one end of the tube. As the displacer progresses along the bed, it pushes all of the adsorbed gases off the charcoal surfaces it encounters. Moving along the bed, each of the gas components displaces all less-strongly adsorbed gases in turn, which results in a progression of purified gases exiting the bed in order of increasing adsorption strength. The purified gases are collected volumetrically or measured with a thermal-conductivity detector.

Displacement was the basis for the so-called natural gas charcoal test used in the 1920s and later,⁵ and was available in the 1940s and early 1950s as an instrument that was produced by at least one company, the Burrell Corp. (Pittsburgh, Pennsylvania, USA).⁶ Today, an instrument such as this one that used boiling mercury

vapours would be a pariah, but at the time it was one of the fastest and most accurate means for determining the contents of natural gas, despite the 8 h analysis time. To the manufacturer's credit, later versions substituted organic vapours for the mercury displacer. Figure 1 illustrates the appearance of a chromatogram from this instrument.⁶ Each of the plateaus represents the period of emergence of a pure gas.

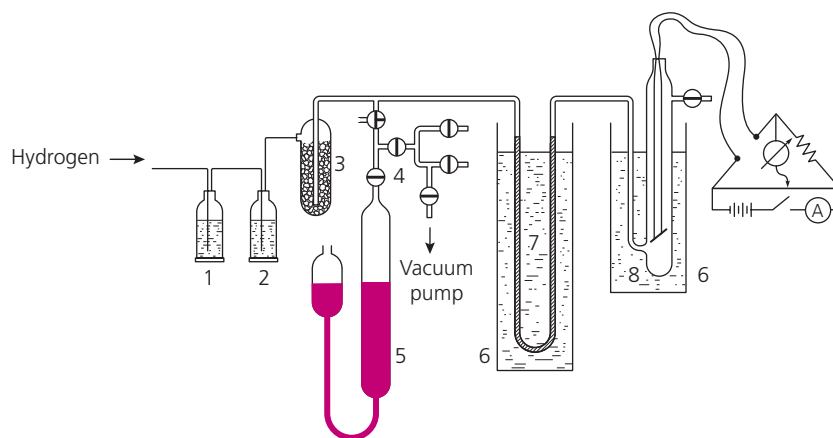
A number of individuals augmented displacement development of adsorbed gases to meet various analytical challenges. One technique, attributed to Paul Schufftan⁷ (1896–1980) of Gesellschaft für Lindes Eismaschinen (Hollriegelskreuth, Germany), used a continuous flow of carbon dioxide across a charcoal bed to enhance displacement of lighter gases by higher fractions. This technique could be described as an early form of elution development. Other researchers, such as Stig Claesson⁸ (1917–1988) of Uppsala University (Uppsala, Sweden) and Courtenay Phillips⁹ (born 1924) of Oxford University (Oxford, UK), developed complex devices and accessories to better control the temperatures, pressures and flows of their analytical systems. These mechanical embodiments, unfamiliar to modern analysts, were marvellous constructions that presaged most of the controls routinely found in present-day GC instrumentation. Ultimately, however, displacement development was itself displaced completely by the meteoric rise of elution gas–liquid partition chromatography

Figure 1: Displacement chromatography recording from the Turner-Burrell adsorption fractometer, circa 1943. Total time: ~8 h; detector: thermal conductivity; sample: 5 L dry natural gas; displacer: mercury vapour; column: 6 ft × 0.75 in. at the entrance, tapering to 0.1875 in. at the exit, packed with charcoal.



Plateaus: 1 = air, 2 = methane, 3 = carbon dioxide, 4 = ethane, 5 = propane, 6 = isobutane, 7 = butane, 8 = pentanes. The signal is redrawn from reference 6.

Figure 2: Schematic of the GC system used in Erika Cremer's laboratory in Innsbruck (1946–1949).¹⁵



1 = permanganate scrubber, 2 = concentrated sulphuric acid scrubber, 3 = adsorbent for gas purification, 4 = sample inlet system, 5 = burette containing mercury with niveau glass used for sample introduction, 6 = thermostat (for the column and the detector), 7 = separation column, 8 = katharometer (thermal-conductivity detector).

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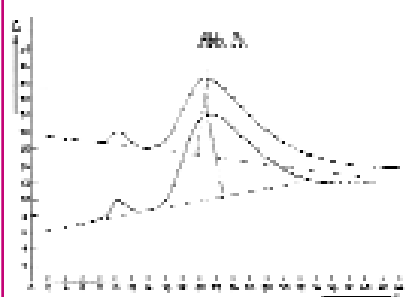
Elution Chromatography

The question arises, then, as to when researchers began to use elution in GC as a conscious choice in lieu of displacement. Although Martin and Synge¹⁰ raised the possibility of elution GC in their well-known 1941 paper about partition chromatography, the text did not see extensive circulation until after World War II. Before that time, solute diffusion in the mobile phase was considered to be a limiting factor that would cause solute bands to mix together in short order and thereby destroy their resolution, a problem not endemic to displacement development. Even so, several individuals began to experiment with elution GC in the early 1940s.

One of these investigators, Gerhard Damköhler (1908–1944) of the University of Göttingen (Germany), perhaps was the first to study systematically the use of a carrier gas in gas–solid chromatography¹¹ and to deduce a number of the fundamental GC relationships.

Gerhard Hesse (1908–1997), working at the University of Marburg/Lahn (Germany), devised an elution gas–solid chromatography system that separated the isomers of various saturated and unsaturated volatile fatty acids on silica gel with carbon dioxide carrier gas.¹² Hesse perhaps was the first to explicitly recognize the connection between his technique and Tswett's liquid–solid adsorption analysis.

Figure 3: The first chromatogram from Cremer's laboratory: the separation of air and carbon dioxide on charcoal.¹⁵ The dots show the individual data points measured and recorded by hand.



In the United Kingdom, Eugene Glueckauf¹³ (1906–1982) investigated solid-adsorption separations of inert and low molecular weight gaseous products of nuclear fission, although his work remained unpublished until 1956 because of its secret nature.

By the end of the war, the stage had been set for additional developments in elution gas–solid chromatography. Two researchers, Erika Cremer (1900–1996) of the University of Innsbruck (Austria) and Jaroslav Janák (born 1924) of the Institute for Petroleum Research (Brno, Czechoslovakia), embarked on activities that resulted in the first instrumental systems that were clearly recognizable as elution GC systems. Those instruments contained all of the principal components that any GC system today includes.

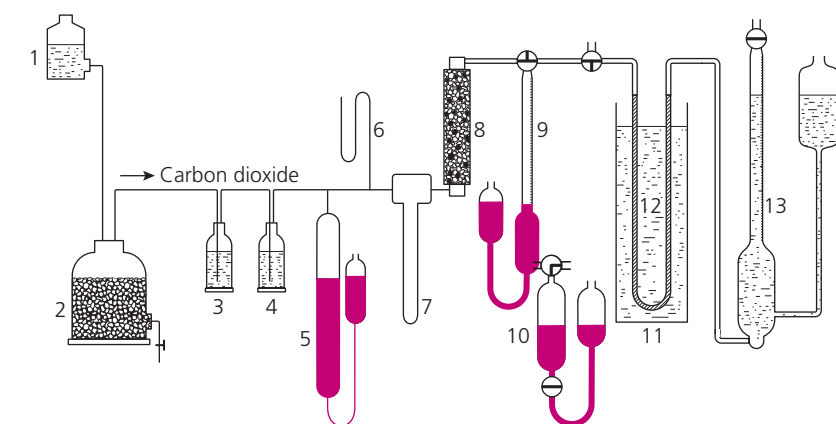
After the war, Cremer was in charge of the Institute of Physical Chemistry at the University of Innsbruck. In 1946, she and her graduate student, Fritz Prior, began investigations to prove her conjecture that gases such as ethylene and acetylene could be separated on the basis of the differences in their heats of adsorption using an elution system. Her idea had been submitted to and accepted by the German journal *Naturwissenschaften* in 1944, but the manuscript was lost, and it was not published until 1976.¹⁴ Prior's work quickly verified her hypothesis, but the publication

of the results was delayed. Another graduate student, Roland Müller, extended the work to include quantitative analysis of small amounts of material, although results remained unpublished until 1951.

Figure 2 is a diagram of the system used by Prior.¹⁵ It might seem surprising to modern gas chromatographers that this piece of equipment could produce useful separations. It is a tribute to Cremer and Prior's skills that they obtained such good results. At that time, the University of Innsbruck had little equipment and no recorders, so they had to write down the signal level at regular intervals and then reconstruct the chromatograms by graphing the individual data points. Figure 3 shows one of Prior's chromatograms.¹⁵

Janák began to work with elution gas–solid chromatography a few years after Cremer and Prior commenced their studies. He was interested in new techniques for the analysis of coal- and coal-tar–based chemical products. Already familiar with the results of Cremer and her co-workers as well as the preceding works of others in displacement chromatography, he set out to build his own system. Janák was an organic chemist, and he decided to collect the eluted gases and determine their quantities volumetrically instead of using a detector. His system, shown in Figure 4, included a pressure regulator and flow-meter, which assisted him in obtaining more-reproducible results.¹⁶ Janák is also credited with pioneering the use of molecular sieves for gas separations.

Figure 4: Schematic of Janák's GC system (1952–1955).¹⁶



1 = hydrochloric acid container, 2 = marble for the production of carbon dioxide, 3 = sodium bicarbonate scrubber, 4 = concentrated sulphuric acid scrubber, 5 = mercury pressure regulator, 6 = mercury manometer, 7 = flowmeter, 8 = calcium chloride scrubber, 9 = gas microburette for sample introduction, 10 = gas sample storage unit, 11 = column thermostat, 12 = separation column, 13 = nitrometer filled with sodium hydroxide or potassium hydroxide.

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GC systems of the Janák design were used routinely in laboratories until the end of the 1950s, most likely because they were easy to construct from standard laboratory equipment and less expensive than the commercial GC instruments that were produced at the time. The commercial systems were technically superior, however, and the Janák chromatographs eventually fell into disuse.

Postscript

By the mid-1950s, the development of gas–liquid partition chromatography by James and Martin¹⁷ had sparked a revolution in GC. The works of Cremer and others finally had been published and were available to most scientists. Researchers in many countries began to use the new partitioning GC separations in a host of application areas, and their activities quickly surpassed the ongoing work in gas–solid separations. And, of course, Marcel Golay's initial investigations of gas–liquid partition chromatography using open-tubular columns had begun.¹⁸ However, the rapid development of gas–liquid partition chromatography would

have been impossible without the previous three decades of research work in displacement and elution gas–solid chromatography.

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How do adsorption and absorption differ?

Adsorption refers to the attachment of a layer of molecules to the surfaces of active substances such as charcoal. Adsorption is distinct from absorption, in which molecules penetrate beyond the surface of a bulk material. To visualize the difference, imagine the burrs of the thistle and similar plants, which have many hook-shaped appendages. When I walk through a field of tall grass and thistle, many of the burrs will be adsorbed onto my clothing; after they are attached to my clothing, the burrs are not free to be blown about by the wind. When I pick the burrs off and discard them they are again free to be moved about until they encounter some other surface. Conversely, if burrs land on a body of water and sink, they are absorbed into the water and do not reside exclusively at the surface.

