

## CHAPTER

### 1

## SUMMARY OF THE HISTORY OF SOIL CHEMISTRY

<b>1.1 The 19th Century</b>	<b>3</b>
<b>1.2 The End of the 19th and the Beginning of the 20th Century</b>	<b>8</b>
<b>1.3 The 20th Century</b>	<b>11</b>
<b>1.4 The End of the 20th and the Beginning of the 21st Century</b>	<b>14</b>
<b>1.5 Conclusion</b>	<b>15</b>

Soil is essential to life. All life supporting ingredients derive, either directly or indirectly, from soil. Plants growing in soil are directly used for food or are fed to animals, which are then used for food. These same plants take in carbon dioxide produced by animals and give off oxygen. Soil and the plants it supports moderate the amount of liquid and gaseous water in the environment by serving as a reservoir controlling its movement. Elements essential to life, even life in water, are released from soil solids and are recycled by soil chemical and biologically mediated reactions. Thus, an understanding of soil characteristics, the chemistry occurring in soil, and the chemical and instrumental methods used to study soil is important.

As the field of chemistry developed, so did the interest in the chemistry of soil. This was natural because the early chemists extracted elements from geological sources and, in the broadest sense, from soil itself. In fact, the development of the periodic table required the extraction, isolation, and identification of all of the elements, many of which are found abundantly in soil.

The total elemental composition of different soils was studied for some time. This involved a great deal of work on the part of chemists because methods for separating and identifying the elements were long and complicated. As knowledge accumulated, the relationship between the elements found in plants and those found in soil became of greater interest. This was sparked by an interest in increasing agricultural productivity.

At the end of the 19th and beginning of the 20th century, much of the theoretical work and discoveries that would be necessary for the further development of soil chemistry were in place. This included the fundamental scientific basis for various types of instrumentation that would be necessary to elucidate more fully the basic characteristics and chemistry of soil.

Toward the end of the 20th and into the 21st century, basic knowledge of soil chemistry was well developed, although much was and still is not understood. Instrumentation had matured and had been married to computers providing even more powerful tools for the investigation of chemistry in general and soil chemistry in particular. Instruments were being combined sequentially to allow for both separation and identification of components of samples at the same time. Instrumentation that could be used in the field was developed and applied.

A time line for discoveries, development of ideas, and instrumentation essential for our present-day understanding of soil chemistry is given in Table 1.1. It is interesting to note that, in some cases, it took several years to develop ideas and instrumentation for studying specific components of soil, such as

**TABLE 1.1. Time Line for the Development of Ideas and Instrumentation Essential to the Understanding of Soil Chemistry**

19th Century	
1800	Discovery of infrared light—Herschel
1835	Spectrum of volatilized metal—Wheatstone
1840	Chemistry and its application to agriculture—Liebig
1855	Principle of agricultural chemistry with special reference to the late researches made in England—Liebig
1852	On the power of soils to absorb manure—Way
1860	Spectroscope—Kirchoff and Bunsen
1863	The natural laws of husbandry—Liebig
End 19th Beginning 20th Century	
1895	X-rays—Röntgen
1897	Existence of electron—Thomson
1907	Lectures describing ions—Arrhenius
1909	pH scale—Sörenson
1913	Mass spectrometry—Thompson
1933	Electron lens—Ruska
1934	pH meter—Beckman
20th Century	
1940	Chromatography (described earlier but lay dormant until this time)—Tswett
1941	Column chromatography—Martin and Synge
1945	Spin of electron (leads to NMR spectroscopy)—Pauli
1959	Hyphenated instrumentation GC-MS

*Sources:*

Coetzee JF. A brief history of atomic emission spectrochemical analysis, 1666–1950. *J. Chem. Edu.* 2000; **77**: 573–576.

<http://www.nndb.com>. Accessed June 3, 2013.

[http://www.nobelprize.org/nobel\\_prizes/physics/laureates/1945/pauli-bio.html](http://www.nobelprize.org/nobel_prizes/physics/laureates/1945/pauli-bio.html). Accessed May 28, 2013.

Gohlke RS. Time-of-flight mass spectrometry and gas-liquid partition chromatography. *Anal. Chem.* 1959; **31**: 535–541.

ions and pH, and to apply them to soil chemistry. In other cases, such as visible and ultraviolet spectroscopy, application was almost immediate. Although tremendous strides have been made in the development of some instrumentation, such as nuclear magnetic resonance (NMR), it is still in its infancy with regard to application to soil chemistry.

## 1.1 THE 19TH CENTURY

The 19th century is considered the century of the beginnings of the application of chemistry to the study of soil. However, foundations for these advances had been laid with the discoveries of the previous century. Antoine-Laurent de Lavoisier, Joseph Priestley, and John Dalton are well-known scientists whose discoveries paved the way for the developments in agricultural chemistry in the 19th century [1,2].

At the end of the 18th century and the beginning of the 19th, Joseph Fraunhofer invented spectroscopy. At that time, spectroscopy was largely used to investigate the spectra of stars [3]. William Herschel discovered infrared radiation that would later be used in infrared spectroscopy to investigate soil organic matter. Also in the early part of the 19th century, Sir Charles Wheatstone was actively investigating electricity. His most prominent work involved the development of the telegraph. But he also invented the Wheatstone bridge, which would become an important detector for chromatography. A lesser known observation was of the spectrum of electrical sparks, which he attributed to vaporized metal from the wires across which the spark jumped. These were important steps in the eventual development of spectrographic methods of studying metals, especially metals in soil [4].

The result of 19th century chemical analysis of soil was twofold. The soil was found to be largely made up of a few elements among which were silicon, aluminum, iron, oxygen, nitrogen, and hydrogen. The second result was that different soils largely had the same elemental composition. Along with this were the investigations of the elemental content of plants and the relationship between those elements found in soil and those found in plants [5]. As these investigations advanced, it became evident that the inorganic components in soil were essential to plant growth and that crop production could be increased by increasing certain mineral components in soil. It did not take too long to determine that ammonia, phosphorous, and potassium are three essentials that, when added to soil, increase plant productivity. At this early point, chemists were largely interested in studying changes in and the activities of nitrogen, phosphorus, and potassium in soil. Two things about these components were discovered. One was that they needed to be soluble to be used by plants, and the second was that not all forms were available to plants.

Although observations about agriculture in general and soils specifically had been made for centuries, it was the chemist Justus von Liebig who is generally credited with the beginnings of the application of chemistry to the

systematic study of soils. That beginning is usually dated as 1840, when Liebig published his book titled *Chemistry and Its Application to Agriculture*. This was followed by *Principles of Agricultural Chemistry with Special Reference to the Late Researches Made in England*, published in 1855, and *The Natural Laws of Husbandry*, published in 1863.

Three ideas either developed by Liebig or popularized by him are the use of inorganic fertilizers, the law of the minimum, and the cycling of nutrients, which foreshadowed the present-day concern for sustainability. One interesting aspect of this is the fact that Liebig is generally cited as being an organic chemist, while his work on soil chemistry, if not wholly inorganic, at least is largely based on or revolves around the characteristics and use of inorganic chemicals. Perhaps Liebig's involvement could be attributed to the fact that during this time, it was widely thought that organic matter was the most important constituent needed for plant growth, that is, that plants got their nutrients directly from the organic matter or humus in soil.

In the middle of the 19th century, Liebig espoused the idea that fields could be fertilized with inorganic compounds and salts, particularly those of phosphate [6]. In addition, other chemicals needed by plants and frequently mentioned by Liebig are sulfuric acid, phosphoric acid, silicic acid, potash, soda, lime, magnesia, iron, chloride of sodium, carbonic acid, and ammonia [7].

During this time, both organic and inorganic materials added to soil were called manure and exactly what was being added is sometimes confusing. Both organic manure from any source and inorganic compounds and salts added to the soil to increase yields were referred to as manures.

Today, manure refers to excretory products of animals and finds its most common usage in reference to farm animals. This organic material was and is used as fertilizer to provide necessary elements for plants. In the past, it was practically the only material readily available for increasing plant or crop production. The general idea, however, is to add something to soil that will improve plant production. Thus, it remains common in popular agriculture literature to find that material added to soil to improve crop production is called manure even if the material is not organic [8,9].

Organic materials were seen as a potential source of plant nutrients and of interest to agricultural chemist and the world at large. Sewage sludge, compost, and indeed any organic material became a potential source of nutrients for plants. There was little or no understanding of microorganism involvement in organic material in general or in manure in particular, and so there was no understanding of the possibility of spreading diseases by using untreated or uncomposted organic matter [10].

One excretory organic product of particular interest and importance, discovered on islands off the coast of Peru by Alexander von Humboldt in 1802, was guano. He studied this product, which became a widely exploited fertilizer material that was transported and sold around the world [11].

One of the important components of guano is ammonia and because of the observed beneficial effect of ammonia on plant growth, there was early interest

in the ammonia content of the organic matter in general and its availability to plants. This led to an interest in understanding the composition of soil organic matter. Unfortunately, full understanding is yet to be had. Organic matter in soil can be extracted and classified in various ways on the basis of the extraction method used, and various components can be isolated. The extracted organic matter can be broken down and the individual parts analyzed. All of this leads to a lot of information but has not led to a great deal of understanding of the molecular arrangement and geometry of soil organic matter, particularly humus.

Humus is what remains after all the organic matter added to soil is decomposed. This seemingly contradictory statement means that the organic matter remaining in soil after decomposition of added organic matter has been synthesized during the decomposition process. Thus, components released during decomposition react to form a new material generally called humus. The most common extraction of organic matter from soil is with base, and this leads to the isolation of humus.

Humus is important in soil because soil must contain humus along with many other diverse components. Humus plays an important role in any soil analysis because it can contain and release both inorganic and organic components. It has groups that can coordinate with transition metals, thus taking them out of solution. It can also absorb and release a wide variety of organic molecules that can affect analytical results. Humus also has a relatively high cation exchange capacity which is important in understanding the chemistry of soil.

Humus has been and is often referred to as a polymer; however, it is not a polymer. It is not a collection of mers such as in polybutene, where butene is the mer and there are many butene mers bonded together. It is rather a complex mixture of different components bonded together. Up to 12 different types or fractions of soil organic matter are recognized. Humus itself can be subdivided into eight fractions depending on the extraction procedure used. Thus, the existence of organic matter, humus, and its various constituents in soil must be recognized and taken into account in any analysis. Organic matter may augment or obfuscate analytical results.

The importance of organic matter and humus was recognized by Liebig as illustrated in his book, *Chemistry and Its Application to Agriculture and Physiology*, which presents the results of the analysis of plants, ash, humus, and soil. This analysis of plants led to the conclusion that plants take up certain elements from the soil ([12], pp. 155–156). Other elements were also found, but the importance, if any, of these was unknown [12].

Included in Liebig's work are 29 pages ([12], pp. 217–246) of the results of the analysis of 47 soils, in some cases including subsoils, which are generally indicated as being 45 cm deep. The analytical results are given as a percentage of the total, which is a logical approach but is somewhat lacking when relating these results to the environment or soils in general. Also, the analyses do not give a picture or results that could be easily related to the productivity of soil.

This, in part, was probably due to the fact that the major constituent of the analysis was silica, which is the major constituent of all soils. The other constituents of soil are important to plants, but their relationship to plant nutrition is not understood.

These soils were described on the basis of their place in the landscape, texture in a general sense, general productivity, and specific crops grown. The components listed in the analytical report were, most often, silica, alumina, iron oxides, manganese, lime, magnesia, potash, soda, phosphoric acid, sulfuric acid, and chlorine. Also included were humus, carbonic acid, and organic nitrogen. Some of these constituents are presented in different ways in different analyses but generally are present in all analyses. Most of the analyses were for soils of England, but analyses of soils from Germany, the United States, specifically Ohio, Puerto Rico, and Java are also included.

Liebig's attempts to use chemical analysis to identify low productivity soils and to differentiate them from highly productive soils were not very successful. Many of Liebig's analytical results were hard to understand in relationship to plant growth and soil chemistry, because it was not until the development of the concept of pH by Sørensen and its application to soil chemistry using the pH meter developed by Beckman that much of what was occurring could be understood [13,14]. However, these studies did lead to the development of the law of the minimum, which Liebig is often credited with inventing and which has been stated in many different ways but is commonly given as

A manure containing several ingredients acts in this wise: The effect of all of them in the soil accommodates itself to that one among them which, in comparison to the wants of the plant, is present in the smallest quantity.

Justus von Liebig, 1863 [15]

Apparently, Carl Sprengel also stated the same or a similar concept as Liebig perhaps at an earlier date. However, from the literature, it appears that Liebig and Sprengel were not on the best of terms and it is unclear as to who originated the idea of the law of the minimum first. On the other hand, Liebig did do a great deal to popularize the law of the minimum, which is why it is mostly associated with him [16].

The law of the minimum is easy to understand on a cellular, molecular, and atomic level and is applicable to all organisms. Organisms cannot grow by producing partial cells and to produce a whole cell they must have all the constituents in the correct proportion. It is not possible to have a functioning cell that does not have a complete cell membrane, complete genetic material, functional mitochondria, and all the other parts of a functioning cell.

A specific example of the law of the minimum on a molecular level is the essential amino acids. The need for essential amino acids in human nutrition shows that one amino acid cannot substitute for another. Substitution of one amino acid for another can lead to disease. This is shown, for example, in sickle

cell anemia, where a substitution in two amino acids leads to a different hemoglobin and a different cell structure [17].

If a sulfur atom is needed for the functioning of an enzyme, none of the elements surrounding sulfur in the periodic table can substitute for sulfur. One of the reasons some elements can be toxic is that they take the place of the correct, needed element, thus making the molecule they are in nonfunctional.

Liebig's original arguments for this law are well laid out in his book, *The Natural Laws of Husbandry*, published in 1863 [8]. Although specific parts of the book are given as the source of some specific ideas, the ideas are, in reality, developed over a number of pages. As with the law of the minimum, the ideas of cycling of nutrients and conservation of soil fertility are covered in the same work over a number of pages. His basic argument is that if soil is to remain productive, farmers must replenish the nutrients they remove from it when they harvest crops.

Along with Liebig, John Way and John Bennet Lawes (a soil chemist) were important agriculturalists of the time, although they are not as well known in chemistry circles. Way and Lawes established the Rothamsted Experimental Station in England and carried out both chemical and field experiments designed to explain the chemistry occurring in soil. Sometimes, they supported and, at other times, were at odds with Liebig. In either case, they were tremendously important in the development of modern agricultural chemistry.

The work of Liebig, Way, and Lawes provided the basic understanding of many of the constituents in soil including both inorganic and organic acids and bases, but not of pH (which was not known at the time). The importance of lime, phosphate, and sulfur was understood, if only incompletely. Sulfur was reported as being applied as sulfuric acid. It is, however, unclear as to exactly how it was applied. John Lawes clearly described the changes in ammonia compounds when they were applied to soil. Unfortunately, he was unable to fully explain what was going on in this process [18]. Regardless, two things about these components were discovered. One was that they needed to be soluble to be used by plants, and the second was that not all chemical forms or species were available to plants.

He also observed and described base exchange in soil, which would later be understood to be cation exchange. However, this understanding had to wait until further development of chemistry and the concepts of ions and exchange reactions.

Along with this were investigations of the elemental content of plants and the relationship between those elements found in soil and those found in plants. As these investigations advanced, it became evident that the inorganic components in soil were essential to plant growth and that crop production could be increased by increasing certain mineral components in soil. It did not take too long to determine that ammonia, phosphorous, and potassium are the three essential components that increase plant productivity. At this early point,



chemists were largely studying changes in and the activities of these components in soil.

During this time, all the prominent scientists and chemists were directly involved in either research and discoveries related to soil chemistry or discoveries that formed the basis for a much deeper understanding of processes occurring in agricultural systems including soils.

However, toward the end of the 19th century, there were still some things about soils and chemistry that inhibited an understanding of much of soil chemistry. The concepts of pH and ions had not yet been developed. Although clay was known and had been known for centuries, the varieties of clays in soil were not known and thus their effect on soil chemistry was unknown. The basic concepts of ion exchange and buffering were also not yet understood either in chemistry or in soils.

## **1.2 THE END OF THE 19TH AND THE BEGINNING OF THE 20TH CENTURY**

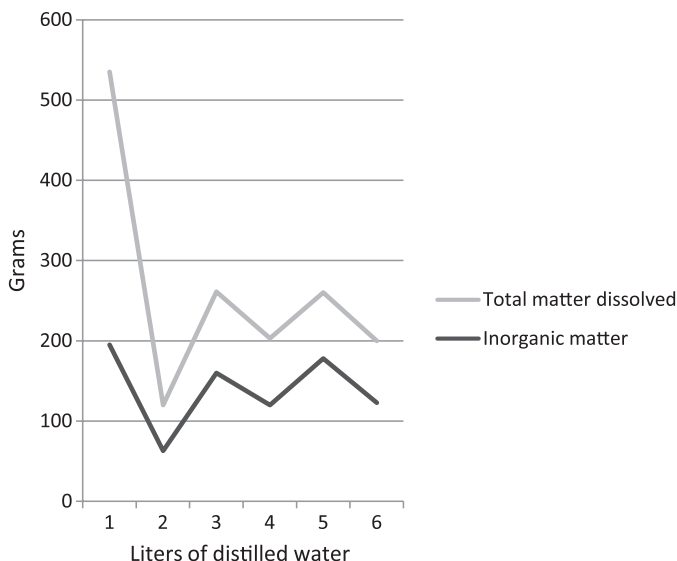
In 1904, King published a rather extensive collection of work regarding the composition of soils and manure [19]. At this time, a number of analyses involved extracting soil with water, often over an extended period of time, analyzing the components extracted, and reporting the results on the basis of 1,000,000 L of water used in the extraction. This represented a useful way of presenting data, which is essentially reporting it as parts per million (ppm). An acre of soil (6 in. or 15 cm deep) is taken as containing either 2,000,000 lb or a hectare 2,000,000 kg. Thus, simply multiplying the amount in 1,000,000 by two gives the amount of a constituent in an acre or hectare.

The results of this type of experiment are illustrated by water extractions conducted by Schultze ([20], p. 328) involving the sequential extraction of soil. Part of the data from this work is graphed in Figure 1.1 and shows the results for six extractions. Only the results for total solids and the inorganic fraction are graphed (other data are given in the table from which these data are taken). The pattern shown is commonly seen in soil extractions even when a contaminant is being extracted. It is to be expected that, with multiple extractions, the level of analyte<sup>1</sup> would constantly decrease and eventually become zero. That does not often happen, but rather, the level of analyte drops to some low level and seesaws around this low level.

Subsequently, E. W. Hilgard took up the cause of soil chemistry. He carried out research using data from King and others in order to find a chemical characterization of soil that would differentiate between productive and unproductive soils. Additionally, soils were extracted with acids of various strengths as indicated by their specific gravity. Results of this type of extraction were expected to indicate the long-term productivity of a particular soil. Also during this time, the concept of a minimum level of a particular component,

<sup>1</sup> The specific element, compound, or species to be analyzed for.





**Figure 1.1.** Total and inorganic matter extracted from soil by water. Adapted from Schultze ([20], p. 328).

for instance, phosphate (reported as phosphoric acid), needed for a soil to be proactive was developed [20].

The transition between the two centuries also saw the discovery and development of two concepts essential to the further development of the understanding of soil chemistry. One was the discovery by J. J. Thomson of the electron, a subatomic particle. This work occurred around 1897 and culminated in the determination of the electron charge-to-mass ratio, which made it possible to develop the idea of ions [21]. This was basic to the concept of ions discussed and developed by Svante Arrhenius in a series of lectures given at the University of California at Berkeley in 1907 [22]. In this series of lectures, he clearly describes ions of hydrogen and chlorine. The basic idea of a hydrogen ion and its application to enzyme chemistry would be further developed by S. Sörenson [13].

Interestingly, previous to Arrhenius's development of the theory of ions, John Way described the exchange process after a series of experiments in which he added potassium chloride to soil and then passed water through it. Potassium was retained by the soil and an equivalent amount of calcium and magnesium was found in the water exiting the soil. The elements retained and eluted from soil were the bases, and so he called this base exchange. Today, we call it cation exchange because we know that the elements are in the form of cations [23]. However, the understanding of this process had to wait until the development of knowledge of ions.

An ion is any species that has lost or gained an electron. Of particular interest and importance are the inorganic ions of nitrogen (i.e., ammonium and

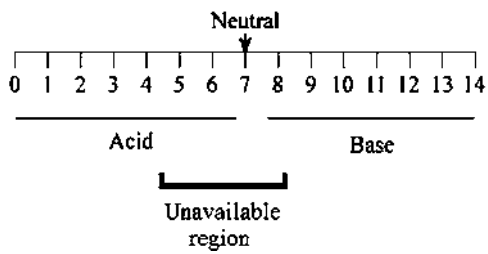
nitrate), phosphate, hydrogen, calcium, and potassium as shown in Figure 1.2. Many organic molecules can and do exist as ions and are important in soil chemistry; however, they have not been studied as intensively as have been the inorganic ions. The development of the concept of ions is essential to the understanding of pH and to understanding ion exchange, particularly cation (positive ion) exchange in soil.

In 1909, Sörenson described the development of the pH scale based on the work of Arrhenius and the characteristics of water. Experiments and the resulting calculations show that water dissociates into hydrogen ions ( $H^+$ ) and hydroxide ions ( $HO^-$ ) and that the product of their concentrations equals close to  $10^{-14}$  ions in aqueous solution. From this, a pH scale from 0 to 14 was developed and the scale describing this relationship using the abbreviation pH was developed (in the older literature [13], one may encounter both the “p” and the “h” capitalized, i.e., as PH). Today, it is universally designated as pH [13,22].

Chemists were limited to determining the pH using litmus paper. Blue litmus turns red at pH 4.5 and red litmus turns blue at pH 8.3. Thus, the region between 4.5 and 8.3 (see Figure 1.3) was unavailable. Many important chemical reactions including conditions affecting the availability of plant nutrients occur in this region of the pH scale. Understanding these important reactions thus

$NH_4^+$	$NO_3^-$	$HPO_4^{2-}$	$H_2PO_4^-$
Ammonium	Nitrate	Hydrogen phosphate	Dihydrogen phosphate
$H^+$	$Ca^{2+}$	$K^+$	$Mg^{2+}$
Hydrogen ion or proton	Calcium	Potassium	Magnesium

**Figure 1.2.** Common important inorganic anions and cations ions in soil.



**Figure 1.3.** The pH scale showing the region unavailable to chemists before the development of the pH scale and the pH meter.

had to wait for the full development of the pH scale and the instrumentation necessary to investigate these pHs.

It would not be until the development of the pH meter and pH electrode that soil scientists had a good way to measure soil pH. In 1934, A. O. Beckman introduced the first pH meter and started a company to build and sell the meter. This sparked an intense study of soil pH and its relationship to plant nutrient availability [14].

Two fundamental discoveries about the structure of the atom and electromagnetic radiation also occurred during this period and provided a foundation for instrumentation that would be fundamental in furthering our understanding of soil chemistry. One was the discovery of X-rays, also sometimes called Röntgen rays, discovered in 1895, by W. Röntgen [24]. The second was made by J. J. Thomson in 1912. He observed positive rays and described how these could be used to identify compounds and elements. Subsequently, he presented a clear description of the process in 1913. This led to the development of mass spectrometry [25].

These discoveries allowed for important increases in the understanding of soil chemistry. The concept of ions and the fact that some elements could exist as ions were an essential step forward. This led to an understanding of the phenomenon John Way clearly described in his work of what he called base exchange, as cited earlier. It led not only to an understanding of ion exchange but also of soil buffering. The discovery of X-rays would eventually lead to the ability to describe and identify soil clays that are the source of much of the cation exchange in soils. The idea of soil pH as opposed to soil being simply acidic or basic based on litmus paper was essential to understanding soil fertility and contamination.

### 1.3 THE 20TH CENTURY

At the very beginning of the 20th century, two very important discoveries or inventions were made. M. S. Tswett discovered and developed chromatography and Fritz Haber demonstrated the chemical production of ammonia. Both of these would dramatically affect soil chemistry. Chromatography provided a method of separating the myriad organic and inorganic compounds and ions found in soil. Development of the Haber process led to the widespread use of ammonia and nitrate fertilizers and the intense study of the chemical changes that nitrogen undergoes in soil.

The development of chromatography was first described by M. S. Tswett and is generally credited to him [26]. He initially separated chlorophylls using a column of calcium carbonate and various solvents. His basic setup for chromatography was, and still is, a stationary phase and a mobile phase. As the mobile phase carries components of a mixture across the stationary phase, they are separated from each other and come out of the setup at different times [27]. The term chromatography came about because the compounds initially

separated by Tswett, the chlorophylls, are colored. The term continues to be used, although most mixtures separated today are colorless. His general method, however, lay dormant until the 1940s.

It was in this time period that A. J. P. Martin and R. L. M. Synge again brought column chromatography to the forefront. Beyond this, they opened the flood gates for the development of various chromatographic techniques with further development of paper chromatography and the development of thin-layer chromatography [28]. All the basic variants of chromatography, elution, gas (also divided into gas-liquid and gas-solid chromatography), ion exchange, thin layer, high-performance, supercritical, capillary electrochromatography, and size exclusion were developed and put to practical use.

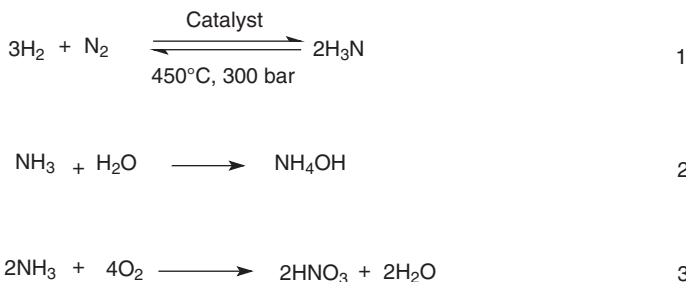
Even though it is sometimes not thought of as a chromatographic technique, we should also include electrophoresis. In this instance, paper or a gel is the stationary phase and electricity is the mobile phase. Although all types of chromatography are in extensive use in all kinds of investigations, electrophoresis has a particular prominence today because of DNA analysis [29].

One particularly important application of chromatography has been to the analysis of pesticides, their degradation and movement. Small amounts of pesticides can be determined and their interaction with soil can be modeled using chromatographic methods [30]. It is unlikely that all types of chromatographic separation have been developed or even conceived. New variants such as ultrahigh-pressure liquid and hydrolytic interaction liquid chromatography are but two examples.

It was well established that nitrogen in a “fixed” form—that is, combined with another atom other than nitrogen—was essential for plants. Before the development of the Haber process for chemically “fixing” nitrogen, the sources of nitrogen fertilizer were nitrogen-fixing plants and bird droppings, particularly guano, mined mostly off the coast of Peru. Nitrogen-fixing plants, the legumes, were used in rotations or as green manure crops to provide nitrogen for subsequent crops. Guano was widely mined and exported as fertilizer all around the world.

In addition to nitrate and other nitrogen compounds, guano contains phosphate and potassium, thus making it a good fertilizer. Deposits of guano were discovered and studied by Alexander von Humboldt in 1802 [11]. This source of fertilizer had thus been known for some time before the development of the Haber process for producing ammonia. However, guano was and is limited and unsustainable as a source of fertilizer for crops, particularly on a worldwide basis.

Although the atmosphere is 78% nitrogen gas ( $N_2$ ), it is not available (i.e., able to be used) to plants or animals except after it has been “fixed.” Thus, the development of the process for making ammonia from hydrogen and atmospheric nitrogen by Haber was extremely important. The first reaction (1) in Figure 1.4 shows the reaction carried out in the Haber process. This reaction is reversible so ammonia is compressed and cooled, and liquid ammonia is removed from the reaction mixture to drive the reaction to the right.



**Figure 1.4.** Reaction and conditions used by Fritz Haber to produce ammonia from hydrogen and nitrogen. The reaction of ammonia with water to form ammonium and the oxidation of ammonia to nitric acid, a common reaction in soil, are also given.

Figure 1.4 also shows two other reactions. In reaction 2, ammonia reacts with water to form ammonium hydroxide. Reaction 3 shows that ammonia can also be oxidized to form nitric acid from which all forms of nitrates can be produced. All three forms of nitrogen (ammonia, ammonium hydroxide, and nitrates in various forms) are commonly found in soil and can be added to soil to supply nitrogen to plants (see also Figure 6.5). This process thus opened up an inexpensive method of producing nitrogen compounds that would be used as fertilizers.

It was during this time, the 1940s, that the spin of electrons and protons was observed by Wolfgang Pauli [31,32]. This discovery would eventually lead to the development of NMR spectroscopy, better known simply as NMR. It is also the basis of magnetic resonance imaging (MRI) [32]. Also during this time, Ernst Ruska experimented with and developed a “lens” that could be used to focus a beam of electrons. This led him to develop an electron microscope with a  $400\times$  magnification [33]. Thus, all the basic knowledge necessary for the further development of our understanding of soil chemistry including the instrumentation needed to explore it was in place at the beginning of the century.

Soil pH differences between pH 4.5 and 8.3, the pHs where litmus changes, could also now be studied and their effect on plants refined. With this knowledge also came the concept of soil buffering and its importance in understanding soil chemistry. A better understanding of the cation exchange of soil was developed. Various extraction procedures were developed to extract specific analytes from soil. One of the questions, which is ongoing, was and is the specificity of extractants, particularly as to the biological activity or availability of the analyte extracted. It was also during this time that experimentation with various phosphate extractants was occurring. The objective was to find an extractant that would extract that portion of phosphate available to plants during the growing season. These ideas, combined with the availability of nitrogen, allowed for the study of nitrogen changes in soil and eventually the understanding of the nitrogen cycle. A much deeper understanding of soil chemistry developed from all of this basic knowledge.

The middle of the century saw the development of instrumentation based on these discoveries and the evolution of functioning instruments that were available from a number of manufacturers. Extracts could be analyzed using these instruments. They were and are constantly being improved in terms of detection, particularly with relationship to sensitivity. Thus, they provide the tools necessary for an even deeper understanding of soil chemistry.

#### **1.4 THE END OF THE 20TH AND THE BEGINNING OF THE 21ST CENTURY**

During the past few centuries, interest shifted from simply determining if something was present in soil to the form or “species” it was in. This was driven by the fact that the form, often, if not always, determines its biological availability, danger, or toxicity. This has been described as “speciation” and is often thought of as referring to the ionic state of the analyte in question. However, it should also be applied to combinations of inorganic and organic compounds and ions and their environments.

A number of advances in instrumentation occurred at the end of the 20th and the beginning of the 21st centuries. Computers were being used not only to acquire signals generated by instrumentation but also to display the data and to manipulate it. As this process continued, they were also used to control instruments and to allow for automatic sample changers to be added to instruments. Autosamplers allow samples to be continuously analyzed even in the absence of an instrument operator. This significantly increases the number of samples analyzed, which greatly increases the amount of chemical information available about a wide variety of soils.

Additionally, with the inclusion of computers as part of an instrument, mathematical manipulation of data was possible. Not only could retention times be recorded automatically in chromatograms but areas under curves could also be calculated and data deconvoluted. In addition, computers made the development of Fourier transform instrumentation, of all kinds, practical. This type of instrument acquires data in one pass of the sample beam. The data are in what is termed the time domain, and application of the Fourier transform mathematical operation converts this data into the frequency domain, producing a frequency spectrum. The value of this methodology is that because it is rapid, multiple scans can be added together to reduce noise and interference, and the data are in a form that can easily be added to reports.

A type of radiation that was not available earlier came into existence and eventually became available to soil scientists. This is the radiation given off by synchrotrons that emit what is called synchrotron radiation (originally considered a waste product of acceleration electrons close to the speed of light). It is described as similar to bright X-rays. This electromagnetic radiation has been used to successfully elucidate the structure and oxidation states of metals in soil and thus their likelihood of becoming environmental pollutants [34].

Once into the 21st century, hyphenated instrumentation (i.e., those that couple two instruments together) became prevalent in laboratories. This is the combination of two or more, often different, instruments. In simple terms, the purpose is to first separate the analyte of interest and then to identify it. This takes place using a sample injected into the combined instruments. The most common of the hyphenated instruments is the gas chromatograph, the output of which is fed into a mass spectrometer to produce a gas chromatography–mass spectrometry (GC-MS) [35].

Other combinations are available. For example, liquid chromatographs connected to mass spectrometers (known as liquid chromatography–mass spectrometry [LC-MS]) are fairly common. Almost any combination of two instruments that can be thought of has been built. In addition, two of the same instruments can be connected so that the output from one is fed directly into the other for further separation and analysis. Examples include two mass spectrometers in an MS-MS arrangement and two different gas chromatography columns connected in a series, known as GC-GC. To keep up with these advances, one needs to have a working knowledge of the fundamental principles involved in the techniques and of the abbreviations used for the various instrumentation methods.

Although field portable instrumentation, which is battery operated and self-contained, has been developed in the past, there has been a resurgence of interest in field portable instruments, some of which are small enough to be handheld.

## 1.5 CONCLUSION

Our understanding of the chemistry of soil in terms of both plant and biological availability of inorganic and organic constituents and in terms of environmental interactions and reactions has increased greatly over the past three decades. The inorganic constituents of soil are well known and easily analyzed. A great many of the organic constituents of soil are known; however, there is still much to learn about their occurrence and reactivity. This is particularly true of humus. New instrumentation and combinations of instruments has led to greater insight into the chemistry of metals, nonmetals, and organic matter in soil. This includes their solubility, movement, and reactions. Modern instrumentation is used to analyze soils and soil chemical reactions not only in the laboratory but also in the field. As instrumentation develops and new instrumentation is discovered and brought to bear on the mysteries of soil, an even greater understanding of soil chemistry will be gained.

## PROBLEMS

- 1.1. Describe the observations made by early soil chemist that led to the understanding that soil possessed cation exchange capacity.



- 1.2. What discovery led to a significant increase in the understanding of soil clays?
- 1.3. Give some examples where the development of chromatography led to an increased understanding of soil chemistry. What is the power of chromatographic techniques?
- 1.4. What is a hyphenated instrumental technique? Give the most common example of such a technique.
- 1.5. Explain why the development of the pH scale was so important in understanding plant nutrition. What did this development “open up” to the soil chemist?
- 1.6. Look up and list the various types of spectroscopy that have been developed. Describe the various parts of the electromagnetic spectrum available to each type of spectroscopy.
- 1.7. Describe the basic characteristics that a field portable instrument must have to be useful in the field.
- 1.8. Explain why Figure 1.1 is important to anyone extracting soil.
- 1.9. Is the importance of organic matter to crop production a new concept? Explain.
- 1.10. Is the concept of sustainability a new concept? Explain.

## REFERENCES

1. <http://www.chemheritage.org/chemistry-in-history/themes>. Accessed May 27, 2012.
2. Moore FJ. *A History of Chemistry*. Charleston, SC: Nabu Press; 2010, pp. 33–82.
3. Brand JCD. *Lines of Light the Sources of Dispersive Spectroscopy 1800–1930*. Australia: Gordon and Breach Publishers; 1995, pp. 37–56.
4. Bowers B. *Sir Charles Wheatstone FRS, 1802–1875*. London, England: Science Museum; 1975, p. 204.
5. Daubeny GGB. Memoir on the rotation of crops, and on the quantity of inorganic matters abstracted from the soil by various plants under different circumstances. *Roy. Soc. (London) Phil. Trans.* 1845; **135**: 179–253.
6. von Liebig J. *Chemistry and Its Application to Agriculture*, Playfair L (ed.). Cambridge, England: John Owen; 1842.<sup>2</sup>
7. von Liebig J. *Principles of Agricultural Chemistry and with Special Reference to the Late Researches Made in England*. London, England: Walton and Maberly; 1855.
8. von Liebig J. *Natural Laws of Husbandry*, Blyth J (ed.). London, England: Walton and Maberly; 1863, p. 2.
9. Brock WH. *Justus von Liebig: The Chemical Gatekeeper*. Cambridge, England: Cambridge University Press; 1997, p. 145.
10. Barker TH. The chemistry of manures. *Trans. Yorkshire Agric. Soc.* 1842; **5**: 31–52.

<sup>2</sup> There are many versions of this book; however, this is the one that has the cited data.

11. Egerton FN. A history of the ecological sciences part 32: Humboldt Nature's Geographer. *Bull. Ecol. Soc. Am.* 2009; **90**: 253–282. Available at: <http://dx.doi.org/10.1890/0012-9623-90.3.253>. Accessed June 3, 2013.
12. Liebig J. *Organic Chemistry and Its Application to Vegetable Physiology and Agriculture*. Philadelphia: J. Campbell; 1845.
13. Sörenson SPL. Enzyme studies II. The measurement and meaning of hydrogen ion concentrations in enzymatic processes. *Biochem. Z.* 1909; **21**: 131–200.
14. <http://www.chemheritage.org/>. Accessed June 3, 2013.
15. Justus von Liebig, 1863. <http://www.todayinsci.com>. Accessed June 3, 2013.
16. Ploeg RR, van der Böhm W, Kirkham MB. On the origin of the theory of mineral nutrition of plants and the law of the minimum. *Soil Sci. Soc. Am. J.* 1999; **63**: 1055–1062.
17. Pauling L. Molecular structure and disease. October 9, 1958. Lowell Lecture, Massachusetts General Hospital, Boston, Massachusetts. Available at: <http://osulibrary.oregonstate.edu/specialcollections/coll/pauling/blood/notes/1958s2.8-ts-02.html>. Accessed May 28, 2013.
18. Way JT. On the power of soils to absorb manure. Consulting chemist to the society. (Second paper). *J. R. Agric. Soc. Engl.* 1852; **13**: 123–143.
19. King FH. *Investigations in Soil Management Being Three of Six Papers Influence of Soil Management upon the Water-Soluble Salts in Soil and the Yield of Crops*. Madison, WI: Author; 1904.
20. Hilgard EW. *Soils, Their Formation, Properties, Composition, and Relations to Climate and Plant Growth in the Humid and Arid Regions*. London: Macmillan & Co., Ltd., 1906, pp. 313–371.
21. Dahl PF. *A History of JJ Thomson's Electron Flash of the Cathode Rays*. London, England: IOP Publishing; 1997.
22. Arrhenius S. *Theories of Chemistry Being Lectures Delivered at the University of California, in Berkley*, Slater T (ed.). London, England: Longmans, Green and Co; 1907, p. 48.
23. Way JT. On the power of soils to absorb manure. *J. Roy. Agric. Soc.* 1850; **ix**(1): 128–143.
24. Glasser O. *Wilhelm Conrad Röntgen and the Early History of the Roentgen Rays*. San Francisco, CA: Norman Publishing; 1993, p. 1.
25. Thomson JJ. Rays of positive electricity. *Proc. R. Soc. A* 1913; **89**: 1–20.
26. Issaq HJ, Berezkin VG. Mikhail Semenovich Tswett: the father of modern chromatography. In Issaq HJ (ed.), *A Century of Separation Science*. New York: Marcel Dekker, Inc.; 2002, pp. 19–26.
27. Ettre LS. Chromatography: the separation technique of the twentieth century. In Issaq HJ (ed.), *A Century of Separation Science*. New York: Marcel Dekker, Inc.; 2002, pp. 1–17.
28. Martin AJP, Synge RLM. A new form of chromatogram employing two liquid phases A theory of chromatography. 2. Application to the micro-determination of the higher monoamino-acids in proteins. *Biochem. J.* 1941; **35**: 1358–1368.
29. Miller DN, Bryant JE, Madsen EL, Ghiorse WC. Evaluation and optimization of DNA extraction and purification procedures for soil and sediment samples. *Appl. Environ. Microbiol.* 1999; **65**: 4715–4724.

30. Helling CS, Turner BC. Pesticide mobility: determination by soil thin-layer chromatography. *Science* 1968; **162**: 562–563.
31. “Wolfgang Pauli—Biography.” Nobelprize.org. 18 Jan 2013. Available at: [www.nobelprize.org](http://www.nobelprize.org). Accessed June 3, 2013.
32. Pauli W. *Collected Scientific Papers*, Vols. 1 and 2, Kroning R, Weisskopf VF (eds.). Hoboken, NJ: Wiley Interscience; 1964.
33. [www.nobelprize.org](http://www.nobelprize.org). Accessed June 3, 2013.
34. Fisher M. Advanced spectroscopy in soil biogeochemical research. *CSA News* 2011; **56**: 4–10.
35. Gohlke RS. Time-of-flight mass spectrometry and gas liquid partition chromatography. *Anal. Chem.* 1959; **31**: 535–541.

### BIBLIOGRAPHY

- Brand JCD. *Lines of Light: The Sources of Dispersive Spectroscopy, 1800–1930*. Australia: Gordon and Breach Publishers; 1995.
- Brock WH. *Justus von Liebig: The Chemical Gatekeeper*. New York: Cambridge University Press; 2002.
- Hilgard EW. *Soils, Their Formation, Properties, Composition, and Relations to Climate and Plant Growth in the Humid and Arid Regions*. London, Macmillan & Co., Ltd.; 1906.
- Issaq H, ed. *A Century of Separation Science*. New York: Marcel Dekker, Inc.; 2002.
- Stoltzenburg D. *Fritz Haber: Chemist, Nobel Laureate, German, Jew*. Philadelphia: Chemical Heritage Foundation; 2005.