

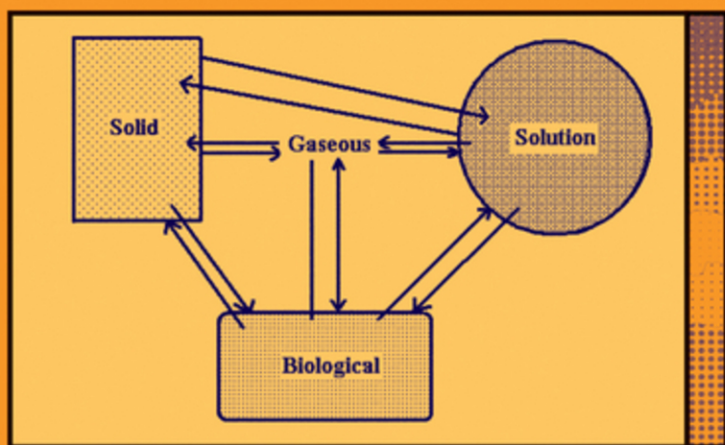
**Chemical Analysis: A Series of Monographs on
Analytical Chemistry and Its Applications**

Mark F. Vitha, Series Editor

Introduction to Soil Chemistry

Analysis and Instrumentation

SECOND EDITION



ALFRED R. CONKLIN JR.

WILEY

Introduction to Soil Chemistry

CHEMICAL ANALYSIS

A SERIES OF MONOGRAPHS ON ANALYTICAL CHEMISTRY
AND ITS APPLICATIONS

Series Editor
MARK F. VITHA

Volume 178

A complete list of the titles in this series appears at the end of this volume.

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Analysis and Instrumentation

Second Edition

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PREFACE

The author is both a soil scientist and a chemist. He has taught courses in all areas of chemistry and soil science, analyzed soil, for organic and inorganic compounds, in both soil solids and extracts, using various methods and instruments, for 44 years. *Introduction to Soil Chemistry, Analysis and Instrumentation, 2nd Edition*, is the result of these 44 years of experience in two distinct climatic zones in the Philippines, four countries in Africa, and one in Central and one in South America. In the United States, this experience includes analysis of soils from all sections of the country.

This book is intended as a reference for chemists and environmentalists who find that they need to analyze soil, interpret soil analysis, or develop analytical or instrumental analyses for soil. Soil scientists will also find it valuable when confronted by soil analyses that are not correct or appear to be incorrect or when an analysis does not work.

There are two themes in this work: (1) that all soil is complex and (2) that all soil contains water. The complexity of soil cannot be overemphasized. It contains inorganic and organic atoms, ions, and molecules in the solid, liquid, and gaseous phases. All these phases are both in quasi equilibrium with each other and are constantly changing. This means that the analysis of soil is subject to complex interferences that are not commonly encountered in standard analytical problems. The overlap of emission or absorption bands in spectroscopic analysis is but one example of the types of interferences likely to be encountered.

Soil is the most complicated of materials and is essential to life. It may be thought of as the loose material covering the dry surface of the earth, but it is much more than that. To become soil, this material must be acted upon by the soil-forming factors: time, biota, topography, climate, and parent material. These factors produce a series of horizons in the soil that make it distinct from simply ground-up rock. Simply observing a dark-colored surface layer overlaying a reddish layer shows that changes in the original parent material have taken place. The many organisms growing in and on soil including large, small, and microscopic plants, animals, and microorganisms also make soil different from ground-up rock.

There are physical changes constantly taking place in soil. Soil temperature changes dramatically from day to night, week to week, and season to season. Even in climates where the air temperature is relatively constant, soil temperatures can vary by 20° or more from day to night. Moisture levels can change

from saturation to air dry. These changes have dramatic effects on the chemical reactions in the soil. Changes in soil water content change the concentration of soil constituents and, thus, also their solubility and reaction rate.

Not only are soil's physical and observable characteristics different from ground-up rock, so also are its chemical characteristics. Soil is a mixture of inorganic and organic solids, liquids, and gases. In these phases, inorganic and organic molecules, cations, and anions can be found. Inorganic and organic components can be present as simple or complex ions. Crystalline materials occur having different combinations of components, for example, 1:1 and 2:1 clay minerals, leading to different structures with different physical and chemical characteristics with different surface functionalities and chemical reactivities.

Organic components range from simple gaseous compounds, such as methane, to very complex materials such as humus. Included in this mix are gases, liquids, and solids, and hydrophobic and hydrophilic molecules and ions. All organic functional groups are included in soil organic matter, and it is common to find polyfunctional organic molecules as well as simple and complex biochemicals. Humus is an example of a complex molecule that contains many different functional groups. Both polyfunctional organic molecules and biochemicals coordinate and chelate with inorganic materials in soils, particularly metals.

The fact that soil always contains water, or more precisely an aqueous solution, is extremely important to keep in mind when carrying out an analytical procedure because water can adversely affect analytical procedures and instrumentation. This can result in an over- or under-determination of the concentrations of components of interest. Deactivation of chromatographic adsorbents and columns and the destruction of sampling tools such as salt windows used in infrared spectroscopy are examples of the potential deleterious effects of water. This can also result in absorbance or overlap of essential analytical bands in various regions of the spectrum.

This *Second Edition* continues the basic approach of the first with the addition of four chapters. Chapter 1 is an outline of the development of soil chemistry with specific reference to the development of instruments that have been essential to the present understanding of soil chemistry. Chapter 7 is a new chapter dealing with soil sampling, both in the field and in the laboratory, soil water sampling, sample transport, and storage. Chapter 8 discusses direct, modified, and indirect methods of soil analysis. Chapter 15 covers the recent development of hyphenated instrumental methods and their application to soil analysis.

Chapters 11 and 12 are the result of separating Chapter 7 from the *First Edition* into two chapters. Chapter 11 deals specifically with the extraction of inorganic analytes and Chapter 12 deals with organic analyte extraction.

All physical and chemical characteristics of soil have a pronounced effect on its analysis. The intention here is to first investigate some of the most important characteristics of soil and its extracts that impact its analysis, as well

INSTRUMENTAL METHOD ACRONYMS

AA	Atomic Absorption
DTA	Differential Thermal Analysis
FID	Flame Ionization Detector
FT-IR	Fourier Transform Infrared (spectroscopy)
GC	Gas Chromatography
HG	Hydride Generator
HPLC	High-Precision Liquid Chromatography or High-Pressure Liquid Chromatography
ICP	Inductively Coupled Plasma
LC	Liquid Chromatography
MS	Mass Spectrometry
NMR	Nuclear Magnetic Resonance (spectroscopy)
TA	Thermal Analysis
TCD	Thermal Conductivity Detector
TLC	Thin-Layer Chromatography
UHPLC	Ultra-High-Pressure Liquid Chromatography
UV-Vis	Ultraviolet-Visible (spectroscopy)
XAS	X-ray Spectroscopy
XANS	X-ray Near-Edge Spectroscopy
XRD	X-ray Diffraction
XRF	X-ray Fluorescence

Common Hyphenated Instrumental Method Abbreviations

Hyphenated Method	Separation Method	Modification	Identification Method
GC-MS	Gas chromatography	None	Mass spectrometry
HPLC-MS	High-precision liquid chromatography	None	Mass spectrometry
LC-ICP	Liquid chromatography	None	Inductively coupled plasma
LC-AAS	Liquid chromatography	Hydride derivatization	Atomic absorption spectroscopy
TA-MS	Thermal analysis	None	Mass spectrometry
DTA-MS	Differential thermal analysis	None	Mass spectrometry
LC-ICP-MS	Liquid chromatography	Inductively coupled plasma	Mass spectrometry
GC-IR-MS	Gas chromatography	Infrared spectroscopy	Mass spectrometry

Abbreviated Periodic Table of the Elements

1 H 1.0																	2 He 4.0	
3 Li 6.9	4 Be 9.0																	9 F 18.9
11 Na 22.9	12 Mg 24.3																	17 Cl 35.5
19 K 39.1	20 Ca 40.0	21 Sc 44.9	22 Ti 47.8	23 V 50.9	24 Cr 51.9	25 Mn 54.9	26 Fe 55.8	27 Co 58.9	28 Ni 58.7	29 Cu 63.5	30 Zn 65.3	31 Ga 69.7	32 Ge 72.6	33 As 74.9	34 Se 78.9	35 Br 79.9	36 Kr 83.8	
37 Rb 85.4	38 Sr 87.6	39 Y 88.9	40 Zr 91.2	41 Nb 92.9	42 Mo 95.9	43 Tc 98	44 Ru 101.0	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3	
55 Cs 132.9	56 Ba 137.3	71 Lu 175.0	72 Hf 178.5	73 Ta 180.9	74 W 183.8	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 196.9	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 208.9	84 Po 209	85 At 210	86 Rn 222	
87 Fr 223	88 Ra 226.0	103 Lr 257	104 Rf 261	105 Db 262	106 Sg 263	107 Bh 262	Lanthanide and Actinide series not shown											

CHAPTER

1

SUMMARY OF THE HISTORY OF SOIL CHEMISTRY

1.1 The 19th Century	3
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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.

Introduction to Soil Chemistry: Analysis and Instrumentation, Second Edition.

Alfred R. Conklin, Jr.

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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—Sørensen
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. 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 analyte¹ 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,

¹ The specific element, compound, or species to be analyzed for.

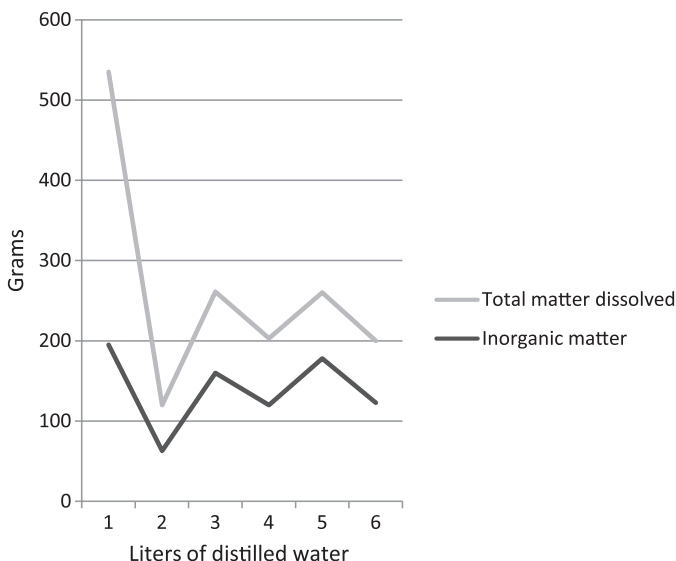


Figure 1.1. Total and inorganic matter extracted from soil by water. Adapted from Schultz ([20], p. 328).

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. Sörensön [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

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.