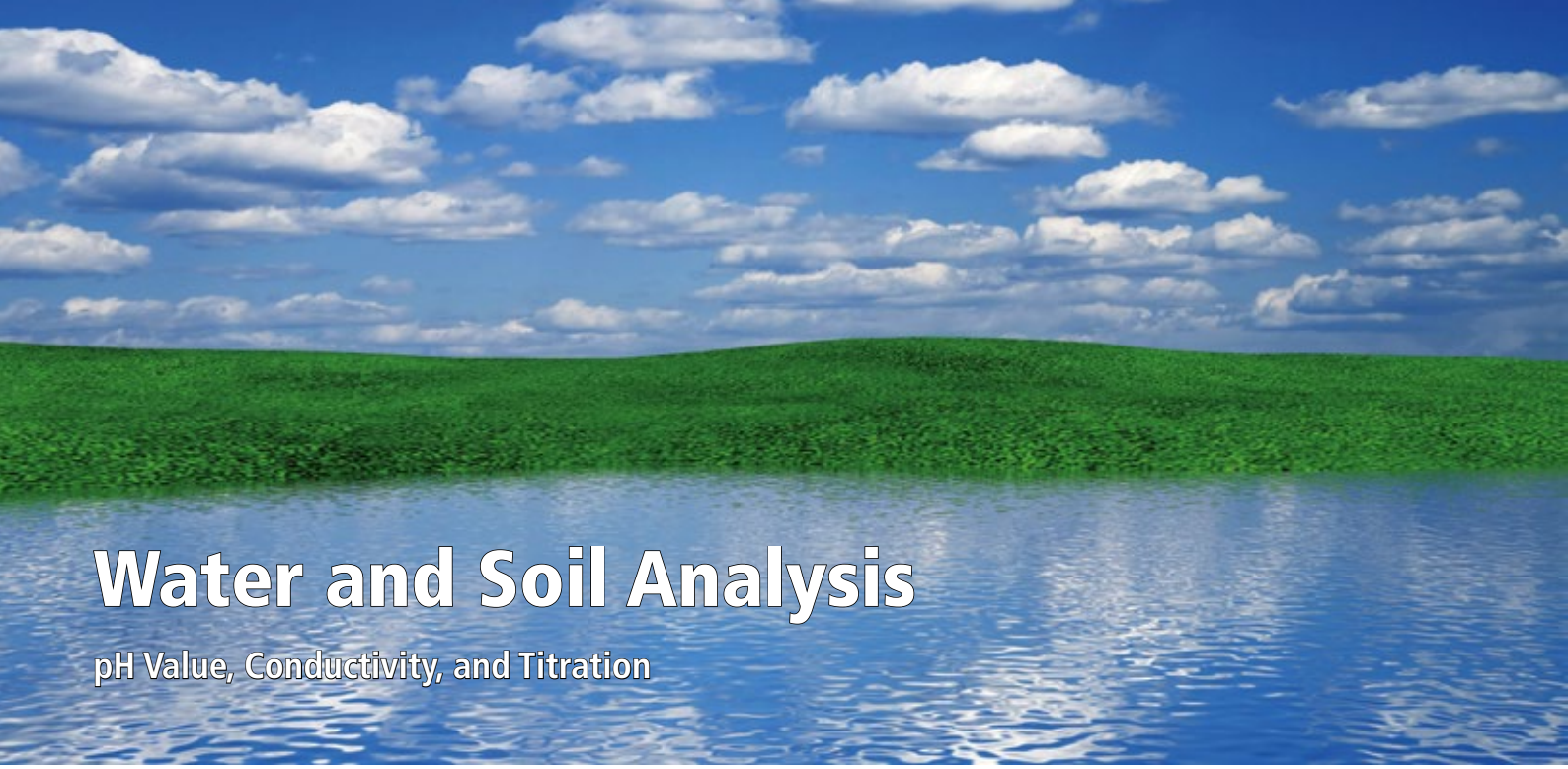

Water and Soil Analysis

pH Value, Conductivity, and Titration

The rapid growth in the world population has led to sharp increases in the consumption of energy and resources and in the production of consumer goods and chemicals. It is estimated that there are a total of 17 million chemical compounds on the market, including as many as 100,000 that are produced on a large industrial scale. A lot of these compounds enter the environment and have to be analyzed.

The Necessity of Environmental Analysis

Substances introduced into the environment are distributed among the environmental compartments water (hydrosphere), soil (pedosphere), rock (lithosphere), and air (atmosphere), as well as among the organisms living on them (biosphere).

The effects of human activities on the environment are complex and call for sensitive analytical methods and powerful analytical instruments. Only if we know the type and quantity of these contaminants, we can protect the environment and its inhabitants. This requires internationally accepted standards, in which limits and test methods are defined.

In this context, the measurement of the pH value and the conductivity as well as titration play an important role. Both pH value and conductivity are parameters that also can be regarded as sum parameters as they characterize similar chemical, physical, or physicochemical features of different components. The pH value is a measure of the acidity or basicity of an aqueous solution and provides important information about chemical and biological processes in the sample. Notably, the pH value allows conclusions about the bioavailability, mobility, and toxicity of pollutants (e.g., heavy metals in soil). The electrical conductivity indicates the amount of dissolved inorganic salts in water (i.e., the salinity) and is thus a fast and inexpensive indicator for estimating the extent of contamination.

Total hardness, alkalinity, acidity, and chemical oxidizability of water components are further important sum parameters that are required for a first risk assessment. In contrast to the directly measured physical parameters, pH value and conductivity, they are mostly determined by potentiometric titration. While the determination of the total hardness and alkalinity implies a complexometric and an acid-base titration, respectively, the determination of the chemical oxidizability of dissolved organic material requires a redox titration of the previously added oxidant. Beyond these examples, titration also includes the analysis of individual components such as ammonia, chloride, fluoride, or sulfide (Table 1 is available online: http://

Fig. 1: The Mati 13 system for the automatic determination of the permanganate index

bit.ly/Metrohm2). Despite the advantages of many instrumental analytical methods, titration has lost none of its appeal. It is a direct, easy, fast, and versatile method with a favorable price that is ideally suited for automation. The reproducible and correct results easily cope with those of the sophisticated methods, for which reason numerous titration methods are cited in international standards.

Just to pick up a few sum parameters, this article looks at the fully automated and standard-compliant determination of the oxygen demand in water samples. Additionally, it describes the direct measurement of the pH value and the electrical conductivity in soil samples.

Water – There is More in It Than We Would Like

As its physical state changes, water passes through all spheres. It is the most frequently analyzed environmental compartment and is also the easiest, because – unlike air or soil – it already exists in the liquid phase.

As a source of food and energy, during use in irrigation, as a solvent, cleaning agent or coolant, and also as a means of transportation and discharge system for effluents, water becomes contaminated with all types of substances. The World Health Organization (WHO) has issued guideline values for about 200 substances found in water. This is why water is the subject of a host of laws, regulations, and standards in most countries (Table 1). If drinking water samples are to be analyzed, sample preparation is usually not necessary; however, it is generally unavoidable in the case of polluted wastewater samples. According to the oxidizing power of the oxidizing agents used, a distinction is made between the permanganate index and the chemical oxygen demand (COD). While the permanganate index is the more informational valuable parameter for samples with minimal or low contamination, COD is suitable for severely contaminated samples.

The Permanganate Index

The permanganate index determines the easily oxidizable fraction of the organic constituents in water and is used, in a broader sense, as a measure for evaluating the organic chemical contamination in waters with minimal or low contamination, such as drinking water samples. For determination according to DIN EN ISO 8467, the water sample is heated for ten minutes with sulfuric acid and an excess of permanganate solution of known concentration in a boiling water bath. After that, the permanganate consumption is determined by adding an excess of sodium oxalate solution and back-titrating the consumed oxalate with permanganate solution (Fig. 2). The permanganate index is expressed as the quantity of oxygen in mg/l that would be needed for oxidation.

Soil – the Complex Multiphase System

The pedosphere is the name given to a highly complex boundary area where hydrosphere, atmosphere, lithosphere, and biosphere coexist. It is a complex multiphase system that consists predominantly of soil mineral matter, approximately equal portions of soil air and soil water, and a small amount or organic matter. It serves as a source of water and nutrients for plants, is a habitat for a large number of organisms, and is an important carbon sink. Harmful substances contained in it come mainly from weathering, cultivation, or the air. Harmful soil pollutants can easily enter the human body through plants and animals. The constituents of soil are very difficult to access and difficult to mobilize. Sample preparation usually involves extraction and digestion procedures (Table 2 is available online: http://bit.ly/Metrohm2).

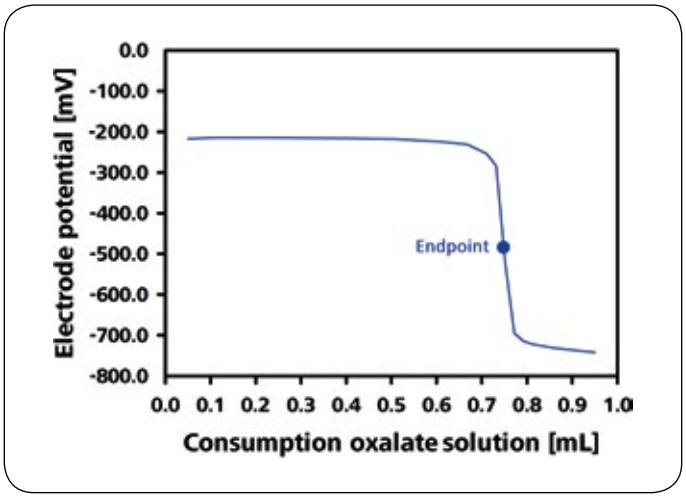

Fig. 2: Titrimetric determination of the permanganate index: consumption of oxalate volume versus measured electrode potential

Soil pH Value

The pH value of a soil sample is the most frequently determined parameter in soil analysis. It is the characteristic value of what is known as "soil reaction," and allows soils to be classified according to their acidity and alkalinity (ISO 10390).

Determination of the pH provides information about the acid or base action of the soil solution. This in turn is of great importance for the nutrient supply and microbial activity of the soil. For example, many metals (trace elements) are considerably more mobile in acid soils. If the soil pH values are very low, toxic levels can soon be reached and these can damage the roots of plants. On the other hand, excessively high pH values quickly lead to a shortage of trace elements because of immobilization.

A simple method for determining the pH value is described in ISO 10390. It describes the slurrying of an air-dried and sieved (max. 2 mm screen) soil sample with distilled water and subsequent measurement. Alternatively, extraction can be performed using 0.01 molar $CaCl_2$ or 1 molar KCl. The cations in these solutions displace the protons that are absorbed on the ion exchangers of the soil as quantitatively as possible.

Electrical Conductivity in Soil Samples

The determination of conductivity provides qualitative information about the amount of dissolved salts in the soil. It enables conclusions to be drawn about the ability of the soil water to mobilize mineral substances in the soil.

To determine electrical conductivity, a weighed-out quantity of a dried soil sample is shaken up with a defined volume of distilled water and then measured directly (ISO 11265).

Conclusion

Every water and soil quality monitoring program consists in determining physical and chemical properties, with the pH value and conductivity being the most important. Besides these direct measurements, titration is a strong tool for the fast and accurate determination of important sum parameters such as hardness, alkalinity, acidity, or oxygen demand. Particularly in complex water and soil samples, the straightforward determination of a single sum parameter often spares the time-consuming analysis of numerous single compounds. However, some cases require the concentration of individual compounds. Also here, titration is the method of choice, from the analysis of ammonium, over the analysis of halides and cyanide to the determination of sulfide, all the more as titration is ideally suited for automation.

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