



Alfred Steinbach

## pH Value, Conductivity and Titration in Water and Soil Analysis

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 analysed.

### 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 can we 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 can also 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



Figure 1: The Mati13 system for the automatic determination of the permanganate index.

water components are further important sum parameters that are required for a first risk assessment. In contrast to the directly measured physical

Table 1				
	Parameter	Standard	Matrix	Method
a) Physical parameters	pH value	EPA 150.1 DIN 38404-5	Drinking water Seawater Wastewater	pH measurement
	Conductivity	EPA 120.1 DIN EN 27888	Drinking water Seawater Wastewater	Conductivity measurement
b) Overall parameters	Alkalinity as $\text{CaCO}_3$	EPA 310.1	Drinking water Seawater Wastewater	Titration
	Chemical oxygen demand (COD)	ISO 6060 ISO 15705 ASTM D 1252 DIN 38409-44 EPA 410.1 EPA 410.3	Drinking water, Seawater, Wastewater	Titration
	Permanganate index	ISO 8467 DIN 38409-5	Drinking water Surface water	Titration
	Ca, Mg (Hardness)	EPA 130.2 EN ISO 9963 DIN 38406-3	Drinking water	Titration
c) Cations and anions	Ammonia	EPA 350.2		Titration
	Chloride	DIN 38405 EPA 325.3	Drinking water Wastewater	Titration
	Free chlorine	EPA 330.1	All types of water	Titration
	Fluoride	ASTM D 3868 EPA 340.2	Drinking water Wastewater	Titration Titration, ISE
	Sulfide	ASTM D 4658 EPA 376.1	All types of water	Titration

**Table 1: Selection of important international water standards for determining physical and overall parameters as well as cation and anion concentrations.**

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 sulphide (Table 1). 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 favourable 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.

### 1) Water — There is More in It Than We'd Like

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

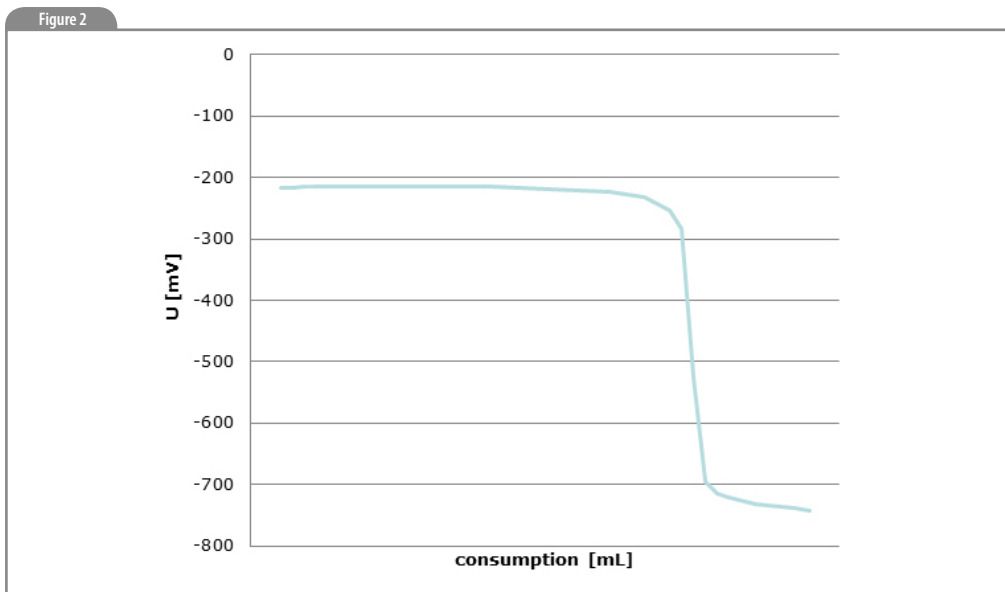
As a source of food and energy, during use in irrigation, as a solvent, cleaning agent or coolant, and also as a means of transportation and discharge system for effluents, water becomes contaminated with all types of substances. The World Health Organization (WHO) has issued guideline values for about 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 analysed, sample preparation is usually not necessary; however, it is generally unavoidable in the case of polluted wastewater samples.

The quality of a water sample can be effectively estimated by measuring its organic pollution load. Several overall parameters are available to this end, and all involve the oxidation of organic matter. 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.

### Permanganate Index According to DIN EN ISO 8467

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,





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

the water sample is heated for ten minutes with sulphuric 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 (Figure 2). The permanganate index is expressed as the quantity of oxygen in mg/L that would be needed for oxidation.

### **Chemical Oxygen Demand According to DIN 38409-44 and ASTM D 1252**

The chemical oxygen demand (COD) is a measured value for the sum of the substances in a certain volume of water that can be oxidized by chromate. Chromate is a much stronger oxidizing agent than permanganate, which is why it also oxidizes most organic compounds practically completely into  $\text{CO}_2$ . In effluent treatment plants, COD is regarded as a valuable indicative parameter for evaluating treatment performance.

For volumetric determination of the COD, the sample of water is heated over a defined period with potassium dichromate. The remaining quantity of potassium dichromate is then back-titrated with ammonium iron(II) sulphate.

The water constituents are oxidized either in a special COD heating device with reflux condensing or in a closed reaction vessel with an external heat source. Titration takes place directly in the reaction vessels without the need

for the content to be transferred to other vessels. This prevents any sample losses and saves valuable time, especially when there is a high sample throughput.

### **2) 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).

### **Soil pH Value — Soil Reaction According to ISO 10390**

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. Determination of the pH provides information about the acid or base action of the soil solution. This in turn is enormously important 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. Moreover, 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 slurring 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  $\text{CaCl}_2$  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.

### **Determination of Electrical Conductivity in Soil Samples According to ISO 11265**

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.

Table 2

Parameter	Standard	Sample preparation	Detection type	Titrant
pH value	ISO 10390	Slurrying	Direct measurement	–
pH value for the determination of the leaching behaviour of inorganic components from waste	DIN CEN/TS 14997	Continuous pH control to determine the influence of pH value on leaching behaviour	Direct measurement (with continuous eluate analysis)	–
Conductivity	ISO 11265	Slurrying	Direct measurement	–
Total organic carbon (TOC), Walkley-Black method	–	K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> /H <sub>2</sub> SO <sub>4</sub> digestion	Visually with barium diphenylamine sulfonate	1 mol/L FeSO <sub>4</sub> (acidic)
Aluminum	–	Extraction	Visually, phenolphthalein	0.02 mol/L NaOH
Carbonate content, Piper method (also known as rapid titration or acid neutralization method)	–	Soil sample is shaken with 0.2 mol/L HCl and allowed to settle; 10 mL of the supernatant solution is back-titrated with NaOH	a) Photometrically with phenolphthalein b) Potentiometrically, SET titration to pH 7.8	0.1 mol/L NaOH
Acidity «Exchangeable acidity» (H + Al)	–	Ion exchange with 1 mol/L KCl	a) Photometrically with phenolphthalein b) Potentiometrically, SET titration to pH 7.6	0.025 mol/L NaOH
Total cyanide and easily released cyanide	ISO 11262	Distillation	a) Photometrically with phenolphthalein b) Potentiometrically	0.005 mol/L AgNO <sub>3</sub>
Soluble anions carbonate/bicarbonate (alkalinity)	–	Extraction with CO <sub>2</sub> -free dist. water	SET titration to pH 8.4 and 4.4	0.1 mol/L HCl

Table 2: Overview of important soil parameters.

## Conclusion

Every water and soil quality monitoring programme 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 sulphide. This is the case all the more as titration is ideally suited for automation.

## References

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**Alfred Steinbach is scientific technical writer and editor in the Marketing Department of Metrohm International Headquarters, based in Herisau, Switzerland. He obtained his Masters in nuclear chemistry from the University of Cologne, Germany, and his PhD in environmental and analytical biogeochemistry from the University of Hamburg, Germany. He joined Metrohm AG in 2006.**