



Article

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Abstract: Potentiometric titration in a fast and simultaneously high-resolution modality was proposed for the identification and quantification of protolytic groups of variable strength at the surface of primary soil particles. The method is implemented by titrimetric data processing as multicomponent spectra (pK_a spectrotitrimetry). Due to the high resolution, the error of acidity-constant assessment (3–5%) is lower, compared to existing approaches; due to the fast titration, the effect of soil hydrolysis is minimized. The soil profiles for acidic Retisols (podzolic soils)—under a spruce crown and in the intercrown space-were studied. These soils, which have similar bulk properties and genesis but developed under different plant covers, were distinguished by pK_a spectral features at 4–5; 5.5–6.5; 6.5-8.5; 7.5-8.5; and 9-10, as well as total group concentrations. Differences in acidic and basicgroup distribution (carboxyl groups, amorphous aluminosilicates, carbonate species, amino groups, soluble (poly)phenolic compounds, phospholipids) and Al and Fe complex compounds within the same soil profiles and between two Retisols were found and quantified. The acidity constants and group concentrations found by pK_a spectrotitrimetry were compared with conventional soilcomposition indicators (total organic carbon, oxalate-soluble Fe and Al, and phosphorus), using principal component analysis. The main correlations are between the concentrations of oxalatesoluble Al and groups with pK_a values of 5.0–6.5 and 8.5; oxalate-soluble Fe and pK_a values of 9.0–10.0; and P_2O_5 and pK_a values of 4.0–6.0 and 6.5–8.5. The method provides a set of major acidity values without a priori information on a soil sample and can be used for screening and identifying similar soils.

Keywords: acidic soils; retisols; podzols; protolytic functional groups; potentiometric titration; acidity constants

1. Introduction

Acidic soils are widespread, including almost all soils in humid areas in northern Europe and Asia. In Russia, these soils occupy more than 50% of the land [1] and are mainly represented by podzols and podzolic soils. These soils are formed in a broad range of climatic conditions, on sandy and loam soil-forming rocks of different mineralogical and granulometric composition. These soils are of low fertility, mainly due to their characteristic low pH values, low organic matter content, geographical location, predominantly in humid (boreal and subboreal) regions, and variable composition, associated with the diversity of soil-forming glacial-fluvio-sedimentary rocks, topography, and vegetation cover. In many regions, they are used for growing industrial and grain crops and forage grasses.

Acidic soil surface properties are connected with compounds of various classes, which are governed by the acid–base properties of their adsorbates and their charges, i.e., surface



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Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). functional groups of primary soil particles [2,3]. In turn, the acid–base state determines the cation exchange capacity of soils, the mobility of chemical elements [4,5], the composition of exchangeable cations, and enzymatic activity, affecting redox processes, complex formation, precipitation, and dissolution. Soil surfaces also contain organic matter, which determines the soil structure, its composition and water resistivity [6–8]. The physical and chemical properties of the surface of soil particles are needed for studies of acidic soils, in addition to understanding changes in the structure and buffering properties of basic clay minerals under the influence of acid or alkaline deposition [9–11]. Moreover, such studies are used to improve the doses in soil liming and the methods for predicting their impact on fertility [12].

At present, at least a dozen of different functional groups is attributed to soil organic protolytic groups: carboxyl; phenolic and alcoholic hydroxyl; carbonyl; quinone; methoxy; ester; amino, amide, and imido; and sulfonic, thiol, and disulfide groups [2,13–15]. Inorganic fragments also serve as a source of formation of surface charge and pH, which usually occurs during the splitting of mineral particles and deformation of the crystal lattices of clay minerals and amorphous minerals [16]. However, despite multiple studies devoted to various aspects of the formation of soil acidity [17,18], the contribution of acid groups and vegetation cover remains insufficiently studied.

Potentiometric acid–base titration of soil suspensions and extracts is a common technique [19–24]. However, the analysis of titration curves is not straightforward in this case, as soil is a multicomponent and polydisperse system, and its components are mostly multifunctional. For both classification and quantification, information on individual components of soil suspensions and extracts is required [25,26]. Their composition is needed to assess the state of the soil cover, as its composition depends on soil and tillage system types [27]. However, the ionization and dissociation constants of these constituents and functional groups are close to each other [28], and most titration approaches cannot identify individual soil components due to the low resolution of titration curves and imperfect algorithms [29]. Thus, titration provides integral parameters only, such as total acid–base buffer capacity [14,30–34] or buffering intensities [28,35–38].

Moreover, the limited capabilities of acid–base titration to determine the type and quantity of acid or basic groups at the surface of primary soil particles are caused by the time between the titrant addition and equilibrium pH measurement, which should be short enough. Although acid–base equilibria are established very fast, soil hydrolysis may lead to its deep dispersion and transformation, which distorts the titration curve [39,40]. Thus, existing acid–base titration approaches are either low-resolution or slow, and therefore are not reliable for finding the detailed composition of soil surface groups.

We propose a high-resolution and at the same time fast potentiometric titrimetry technique, which maximally details the titration curve, while shortening the analysis time, thus decreasing the amounts of hydrolysis products. This technique is implemented in the form of pK_a spectrometry (spectrotitrimetry), i.e., using the processing of the resulting continuous titration curves as arbitrary multicomponent acidity spectra. The technique was previously used for the concentrations and pK_a values of ionogenic groups of mono- and polyfunctional polyelectrolytes: polyacrylic and polymethacrylic acids, gelatin, and humic substances [41–44]. However, so far, it has not been implemented to whole soil samples due to the lack of instruments capable of acquiring high-resolution titration curves at the required speed.

In this study, this technique is used to determine the protolytic groups at the surface of particles of two podzolic soils [45] (Russian soil classification) or Retisols (WRB classification). These soils were selected due to their wide distribution in the taiga region of northern Europe (Finland and Sweden), Canada, and the European part of Russia. The aim of this study was to apply the technique of fast high-resolution pK_a potentiometric titrimetry for identifying and quantifying the organic acidity functional groups in acidic soils.

2. Materials and Methods

2.1. Area Description and Soil Sampling

The studies were carried out in Ust-Kulomsky District of Komi Republic (middle taiga), on Zhezhim Parma hill, in a blueberry native old spruce forest (Figure S1, Supplementary Information). The mean annual air temperature is from +0.2 to +1.3 °C. The amount of annual precipitation is from 670 to 790 mm [46]. The profile of albic Glossic Retisol (Siltic, Cutanic) (Retisol I, RI) was studied at intercrown (open) space on a distance of approximately 4 M from the crown of the spruce. The soil profile of albic Ferric Retisol (Siltic, Cutanic) (Retisol II, RII) was opened under the crown (1 M from the stand) of a 260-year-old spruce (*Picea obovate* Ledeb.). Soil classification is given according to WRB (2022). The distance between pits is about 10 m. Samples were selected for chemical analysis from each genetic horizon. Samples were collected in 2014. For more information, photographs of the spruce forest, where the profiles were opened and studied, and the soil profiles are presented in Figure 1 and Table 1. Air-dried samples were ground and sieved through a 1 mm sieve. More detailed information on the characteristics of the research objects was previously published [47].



Figure 1. Photographs of vegetation and profiles of the studied soils: (**a**) albic Glossic Retisol (Siltic, Cutanic) (RI); (**b**) albic Ferric Retisol (Siltic, Cutanic) II (RII).

Soils	Coordinates	Location	Soil Profile		
RI	N 61°45′43.6″	The intercrown space	Vaccinium myrtillus,The intercrown spaceGymnocarpium dryopteris, Equisetum sylvaticum, Carex globularis.		
RII	$E 54^{\circ}17'50.1''$ h = 260	Spruce crown (260 years old)	Hylocomium splendens, Equisetum sylvaticum, Vaccinium myrillus, Pleurozium schereberi	Oi–Oe–Oa–E/Eh– BELc, i–Btw–C	

Table 1. Description of the research objects.

2.2. General Soil Analysis

Samples were air-dried, and living roots and all particles with a diameter over 1 mm were removed by dry sieving. Organic samples (Oi, Oe, Oa) were ground with a sample grinder WCG75 (Pro Prep, Torrington, CT, USA). Chemical analysis of the soils was performed in the Ecoanalit laboratory and the Soil Science Department of the Institute of Biology, Federal Research Center, Komi Research Center of the Ural Branch of the Russian Academy of Sciences (IB FRC Komi SC UrB RAS). The total contents of carbon (Ctot) and nitrogen (Ntot) were determined by dry combustion on an EA-1110 CHNS-O analyzer (Carlo Erba, Cornareda, Italy). Exchangeable cations were determined by displacing with 1 M KC1, followed by atomic-absorption determination with a Hitachi 180-60 instrument (Tokyo, Japan). The pH values were determined on an Anion-4100 ionomer (Moscow, Russia) at a soil-to-water ratio of 1 (w):2.5 (v) for mineral horizons and 1 (w):25 (v) for organic horizons, respectively [48]. The particle size distribution was determined by the pipetting method, according to Kachinsky, with dispersion and boiling in the presence of NaOH, according to the Russian State Standard (GOST 12536-2014, Soils. Methods of laboratory granulometric (grain-size) and microaggregate distribution). Oxalate-soluble compounds of iron and aluminum were extracted by the Tamm method [49], and dithionite-soluble iron compounds by the method of Mehra and Jackson [50]. The total elemental analysis was determined with a ReSpect energy-dispersive X-ray fluorescence spectrometer (LLC Technoanalytdevice, Moscow, Russia). Phosphorus was determined by inductively coupled plasma atomic emission spectroscopy (ICP SpectroCiros CCD, Spectro Al, Kleve, Germany).

All weighing was carried out on an Ohaus Adventurer Pro AV313C analytical balance (Parsippany, NJ, USA). Glass and plastic chemical workware were used. The autosampler of the AT-710M titrator had 7 positions for beakers: position 1 was used for washing and cleaning the working part of the titrator after each titration; the remaining six positions were used for test samples (volume of vessels, 150 mL, selected for the optimum soil weighed portions of 3 g).

2.3. Reagents and Solvents

Distilled water was used to prepare the reagents and wash the workware. Working solutions of HCl and NaOH were prepared from ampouled reference samples every week; the solutions were stored in closed polypropylene containers connected to the titrator instrument. The titration reagent was collected automatically by the instrument software command. Preparation of saline solutions of acids and titrants was carried out similarly: 0.1M NaOH was prepared from ampouled reference samples and dry NaCl (5.85 g NaCl for a volume of 1 L).

Solutions of 1 M KC1 (puriss.) and 1 M CH₃COONa (puriss.) were prepared from weighed portions of 75.5 and 82.0 g, respectively, in 1.000 L of water. All solutions were prepared in volumetric flasks with a volume of 1 L. The solution of 0.1 M H₃BO₃ was prepared from 6.18 g of a dry sample: a 0.1 M solution of H₃PO₄ from 5.2 mL of conc. acid (density, 1.88 g/cm³) in 1 L of water or 1 L of 0.1 M NaCl. A 0.1 M solution of borax

was prepared from 38.1 g of $Na_2B_4O_7 \cdot 10H_2O$ in 1 L of water. The solution of NaCl was prepared from a 5.8 g weighed portion per 1 L of water.

Kaolinite, $Al_4Si_4O_{10}(OH)$, was taken from the Prosianovskoye field (Ukraine). It contains 39.5% Al_2O_3 , 46.5% SiO₂, and 14.0% H₂O. Air-dried kaolinite was ground, sieved through a sieve (diameter, 1 mm), and stored in a stoppered polyethylene container.

2.4. Titration

All potentiometric titrations were made with a KEM AT-710M (Kyoto Electronic Manufacturing, Kyoto, Japan) automatic potentiometric titrator with a pH electrode (KEM Glass electrode C-171) and a CHA-700 autosampler (both, Kyoto Electronic Manufacturing, Kyoto, Japan). This instrument tracks the real-time response of the system to the addition of a titrant in various modes of titrant supply and equilibration time, with continuous output of results to screen and files. The instrument was operated in the incremental mode, when the titrant is added in small equal portions, with a given time to establish the equilibrium after each portion. Titration was carried out with a titrant aliquot of 0.02 mL, every 3 s, with stirring at a rate of 7 (within the instrument stirrer rate range from 1 to 10), with continuous pH measurement. The volume of 10 mL (25 mL for the Oe horizon of R II soil) of titrant was used, thus obtaining 502 pH points for a titration curve. The difference between adjacent points on the titration curve corresponds to hundredths of pH units. To immerse the working part of the instrument into the test sample, at least 80 mL of liquid is required. A single titration took 45 min.

2.4.1. Model Solutions

Verification of the mathematical program described previously [41] was carried out by the titration curves of model mixtures of polybasic acids (S1, 0.0125 M HCl; S2, 0.00625 M H_3PO_4 and 0.00625 M H_3BO_3 ; S3 0.00375 M H_3PO_4 and 0.00875 M H_3BO_3 ; and S4, 0.00875 M H_3PO_4 and 0.00375 M H_3BO_3). All solutions were prepared in 0.1 M NaCl. Titration of acid model mixtures was made according to the following scheme: to 10 mL of acid or a mixture of acids, 70 mL of 0.1 M NaCl was added, and the mixture was titrated with 0.1 M NaOH, prepared with 0.1 M NaCl.

2.4.2. Kaolinite

A weighed portion of kaolinite of 3 g was mixed with 80 mL of 0.1 M NaCl. Next, the electrode, the mechanical stirrer, and the feeding tube of the titrant were immersed into the solution, and the sample was measured for 5 s without titration to establish the equilibrium and to measure the initial pH value of the soil suspension with enough precision. The suspension was then titrated with 0.1 M NaOH with 0.1 M NaCl.

2.4.3. Soils

A weighed portion of the soil of 3 g was mixed with 80 mL of 0.1 M NaCl. Titration was made with 0.1 M NaOH prepared with 0.1 M NaCl, similarly to kaolinite titration. To determine hydrolytic acidity, 1 M CH₃COONa extracts with pH 8.2 were prepared for a soil-to-solution ratio of 2:5, shaken for 1 h, filtered through a dry folded filter, and titrated with 0.1 M NaOH. Material from poorly mineralized forest litter was not analyzed.

2.5. Data Treatment

2.5.1. Titration-Curve Treatment

The algorithm for computation of the amounts of the acid groups in the soil samples was as follows [41]. Considering a sample as a mixture of monoprotic acids HA_i , with acidity constants K_i , the charge neutrality of the solution titrated with NaOH is

$$\sum_{i} \left[\mathbf{A}^{-} \right] = \left[\mathbf{H}^{+} \right] - \left[\mathbf{O}\mathbf{H}^{-} \right] + \left[\mathbf{N}\mathbf{a}^{+} \right]. \tag{1}$$

Equation (1) can be written as follows:

$$\frac{V_0}{V_0 + V_t} \sum_i c_i \frac{K_i}{K_i + [\mathrm{H}^+]} = [\mathrm{H}^+] - K_w [\mathrm{H}^+] + c_t \frac{V_t}{V_0 + V_t}$$
(2)

Here, V_0 is the initial volume of the solution, V_t is the titrant volume, K_w is autoprotolysis constant of water, c_t is the titrant concentration, and c_i is the concentration of the *i*th acid. Specifying a set of K_i (i = 1, ..., m) and taking given values of c_0 , V_0 , c_t and experimental values of V_t and [H⁺] for n > m points of the titration curve, we get an overdetermined system of *n* equations of (2) linear with respect to c_i solved by the algorithm of linear-regression analysis with restrictions on non-negativity of the solutions [51].

The data obtained in the course the titration was transferred from the AT-710 standalone unit to the computer. The computation algorithm, Equation (2), was implemented as Microsoft Excel scripts. The user imports the following data: the titration curve represented as two columns, the initial system volume, titrant concentration, and the value of the activity coefficient of a mono-charged species. The operator also enters the discrete pK_a values, which will be included in the calculated pK_a spectrum.

We used a p K_a range of 2–13 for the model systems and 4–10 for real soil samples. The step was 1 or 0.5 [41–44]. Contents of groups with p K_a equal to 5.0; 6.5; 8.5; 9.0; and 10.0; or ranges 4.0–5.0; 4.0–6.0; 5.5–6.5; 6.5–8.5; 7.5–8.5; and 9.0–10.0 were determined by potentiometric titration of all the horizons.

2.5.2. Principal Component Analysis

Principal component analysis was made with STATISTICA 8.0 software (TIBCO, Santa Clara, CA, USA). All the test variables were continuous. The original data matrix is centered and normalized to standard deviations. Prior to analysis, a Kaiser–Meyer–Olkin (KMO) test was used; the value was KMO = 0.6, which shows that the data are suited for factor analysis [52]. The decomposition was performed using NIPALS as the most standard algorithm providing the minimum numbers of ambiguous alarms and missed alarms [53,54], with the maximum number of iterations of 50 and a convergence criterion of 0.0001. The number of components describing the source set was selected using the cross-validation by the *v*-fold method; *v* was equal to 7, which provided the minimum error rate of the following PCA procedure and algorithm efficiency [55]. For most treatments, the first two principal components are selected, which describe 65% of the initial data.

3. Results and Discussion

3.1. Morphological and General Soils Properties

The studied Retisols have typical morphological and chemical properties [56]. The organic horizon was typical for boreal forests and was divided into three subhorizons with different organic matter decomposition levels: Oi, Oe, and Oa. An eluvial albic horizon (E) is located under the organic horizon. The upper part of E was infiltrated by total carbon (Eh). The transitional subeluvial horizon (BEL), with albeluvic glossae, was next. Clearly differentiated texture horizons (argic) occurred under the eluvial part of the soil profile. These had a typical multiordinal structure and numerous cutans at the faces of individual particles. R II soil is characterized by a significant increase in nodules in the middle part of the mineral horizons. This increase is probably associated with stem waters enriched in iron, aluminum, and organic matter, which entered the mineral horizons in significant quantities over several centuries [57]. The soil carbon concentration at organic horizons varied from 35.8 to 46.2% (Table 2). The upper mineral horizons contain significantly less carbon. The upper part of the eluvial horizon is characterized by a carbon content of 2.0 to 3.2%; in the lower horizons, the carbon concentration decreases to 0.1-0.9%. The lowest pH values were observed in the organic horizons, where the pH values varied from 4.0 to 5.2. The most acidic were the lower part of the organic horizon (Oa) and the upper part of the eluvial horizons (E). The studied soils have similar soil texture and a weak profile differentiation of texture fraction contents.

Horizon Depth, cm Fraction,	рН		Hydrolytic Acidity,	Exchangeable Cations, mmol/kg		C _{tot} ,	N _{tot} ,	C:N	Oxalate Soluble, %	
%	Water	Salt	mmol/100 g	Ca	Mg	. /0	/0		Fe ₂ O ₃	Al ₂ O ₃
		R	etisol I (intercrov	vn space)						
Oi 0–3 —	4.6	3.9	58.8	21.4	7.8	44.2	1.63	32	—	
Oe 3–6 —	4.3	3.3	56.3	15.7	2.98	43.2	1.9	27	—	—
Oa 6–8 —	4.0	2.9	73.7	11.4	3.03	35.8	1.58	26	—	—
E1 6–11 11	3.9	2.9	14.9	0.60	0.28	2.20	0.148	17	0.18	0.28
Eh 11–14 13	4.1	3.3	5.93	0.71	0.32	3.20	0.22	17	1.27	0.54
E2 20-30 8 30-40 8	4.9 5.0	3.8 3.8	8.83 8.28	0.57 0.50	0.210 0.243	0.41 0.21	0.046 0.030	10 8	0.66 0.35	0.44 0.29
40–50 10	5.3	3.8	6.69	1.17	0.77	0.17	0.024	8	0.28	0.24
BEL* 50–60 13	5.3	3.8	6.53	2.44	1.68	0.12	0.021	7	0.28	0.26
BEL** 60–70 24	5.5	3.8	5.48	8.3	3.40	0.12	0.024	6	0.3	0.27
24	5.6	3.8	4.92	9.4	4.3	0.11	0.024	5	0.29	0.31
80–90 26	5.7	3.9	4.23	10.4	5.6	0.14	0.030	5	0.27	0.27
90-110 28	5.8	4.0	3.71	11.5	5.9	0.13	0.021	7	0.28	0.26
Btw2 110–125 30	6.0	4.1	3.40	12.0	6.1	0.14	0.025	7	0.23	0.24
Cg 130–140 26	5.7	4.1	3.05	12.1	6.2	0.13	0.025	6	0.22	0.22
140–150 28	6.1	4.2	2.74	11.6	6.0	0.11	0.025	5	0.21	0.21
Retisol II (under the crown of spruce)										
Oi 0–2 —	5.2	4.5	50.3	32.1	7.9	45.7	1.8	30		—
Oe 2–4 —	4.8	4.0	60.2	25.0	5.1	46.2	1.9	28		—
Oa 4-6 —	4.1	3.1	88.2	10.8	2.50	41.8	1.7	29		_
E 6–10 13	4.0	3.1	14.9	0.63	0.32	2.0	0.125	19	0.3	0.34
Eh,c 10–20 11	4.3	3.5	16.9	0.76	0.32	2.0	0.128	18	1.28	0.54
BELc,i 20–30 17 30–45 22	4.5 4.8	3.6 3.8	16.9 15.5	0.73 0.99	0.31 0.50	2.1 0.91	0.138 0.074	18 14	1.22 0.92	0.7 0.75
Btw1 45–60 26	5.1	3.7	13.9	2.28	1.54	0.29	0.033	10	0.52	0.6
Btw2 60–80 27	5.3	3.8	10.1	6.5	3.40	0.29	0.038	9	0.44	0.49

Table 2. Physicochemical properties of studied soils.

3.2. Titration-Curve Treatment Selection

When selecting a method of direct potentiometric titration for Retisol samples, the continuous variant [34,38,58,59] was selected over the equilibrium method [22,60], as the former is based on the sequential addition of the titrant to the test soil sample and, due to the shorter equilibration time, it makes it possible to investigate the composition of protolytic groups of the surface of primary soil particles [61].

The following methods of analyzing the potentiometric titration curves of soils are used: (*i*) the calculation of the area under the titration curve to estimate the buffering intensity and calculate the cation-exchange capacity [34,62]; (*ii*) simulation of the experimental data with titration curves, calculated for a set of possible individual soil components with known composition and acid–base properties [63]; and (*iii*) processing titration curves to find acidity constants of individual functional groups and to estimate their quantities. The latter two methods form complementary—direct and inverse —computational problems and usually serve as generalized models implemented in so-called acid–base calculators. Such calculators allow both simulating the titration curve for a given system and experimental technique and calculating the number of components different in acidity constant

(strength) from the actual titration curve [64,65]. However, they reliably calculate the quantities and acidity constants only for a set of not more than four components, which is not suitable for soils. Volk and Jackson [66] proposed a model approach to identify four acidbase buffering ranges, each of which was attributed to specific soil components appearing in the solution in the corresponding pH range: H_3O^+ ions and monomeric Al^{3+} species, polymeric hydroxy-aluminum ions, and other components. The number of components used in the model approach limits the ability to interpret the composition of the system under study. Apart from this study, there are no specialized programs developed directly for the analysis of soil acidity.

A more general approach, which was implemented in this study, describes titration curves as arbitrary acid–base systems without a need of imposing restrictions on the number of components [41–43]. The result of the calculations is a pK_a spectrum—the dependence of the number of groups on their pK_a values specified with a certain ΔpK_a step. Garmash and Vorob'eva [43] showed that the adequacy of the calculation results is achieved with a pK_a step of at least 0.5.

3.3. Initial Tests of Model Systems

For the initial tests of the titration in the selected mode, the verification of the capabilities of the instrument, as well as the parameters of correctness and reproducibility, simple titration models were selected. They are acids and mixtures of acids of different strengths. We have selected HCl, H₃BO₃, and H₃PO₄ as acids with stepwise constants over a wide range. The choice of these model acids was also due to the presence of a wide acidity range of functional groups in soils [19–24]. The titration curves of mixtures of weak acids make it possible to check the correctness of the calculation algorithm [41], which was applied subsequently to the treatment curves titration of the soil samples. The titration of the soil samples was carried out using a saline solution with an ionic strength of 0.1 M because this ionic strength is close to that of soil solutions. The curves obtained are presented in Figure S2 (Supplementary information). For 0.0125 M HCl, the concordant concentration value of 0.01245 M was calculated. Table 3 summarizes all non-zero values of pK_a calculated for H₃BO₃/H₃PO₄ mixtures with a step of 0.5. The second line for each mixture in Table 3 shows (in bold) the total concentration of groups with adjacent pK_a.

Table 3. The pK_a values of real titration curves of model acid samples. The total concentrations of groups with adjacent pK_a are in bold.

A 11361 4	pK _a							
Acid Mixture	2.5	3.0	6.5	7.0	7.5	9.0	9.5	10.0
0.00625 M H ₃ PO ₄ and 0.00625 M H ₃ BO ₃	0.00388 0.00	0.00269 0657	0	0.00439 0.00640	0.00200	0.00000	0.00619 0.00619	0
$0.00375 \text{ M H}_3\text{PO}_4$ and $0.00875 \text{ M H}_3\text{BO}_3$	0.00248 0.00	0.00135)383	0.00033	0.00299 0.00332	0.00000	0.00384	0.00449 0.00833	-
0.00875 M H ₃ PO ₄ and 0.00375 M H ₃ BO ₃	0.00634 0.00	0.00278)912	0.00000	0.00602 0.00888	0.00286	0.00000	0.00314 0.00381	0.00067

The value for pK_a of 2.5–3.0 is concordant with the concentration of phosphoric acid in the first dissociation stage (pK_a 2.15). The amounts for pK_a of 7.0 and 7.5 are in agreement with the concentration of phosphoric acid in the second dissociation stage (pK_a 7.2). Finally, a sum of concentrations for pK_a of 9.0 and 9.5 describes boric acid by its first dissociation stage (pK_a 9.15). Thus, in all the cases, the calculations agree well with the composition of the model mixtures (Table 3).

3.4. Kaolinite

Kaolinite, as a mineral of the layered silicate subclass, a widely distributed secondary mineral present in the clay fraction of many soils [67,68], previously applied to model

soils [69], was a transitional step from analyzing aqueous acid mixtures to soil analysis. For a ΔpK_a step of 1, the pK_a range values are 6.0–7.0 and 9.0–10.0 (Figure 2a), which agrees with existing the acidity constants of kaolinite of 6.9 [70] and 8.0 [71]. However, despite the fact that the titration curves of kaolinite (Figure S3, Supplementary Information) differ insignificantly visually, the calculations at this ΔpK_a step result in a significant difference between replicate curves, which is inappropriate. As ΔpK_a affects the accuracy of processing, a smaller division was tested. Garmash, Ustimova, Kudryavtsev, Vorob'eva, and Polenova [41] recommended a minimum ΔpK_a step of 0.5. At a ΔpK_a of 0.5 applied for the same experimental curves (Figure 2b), three types of groups with pK_a ranges of 6.5–7.0; 8.5–9.5; and 10.0 can be identified clearly and reproducibly.



Figure 2. Molar distribution of protolytic functional groups (FG) for kaolinite with pK_a steps (**a**) 1, (**b**) 0.5, and (**c**) 0.25; for (**a**), errors are shown, for (**b**,**c**), replicates are shown individually.

At the same time, the proposed method of titration-curve processing provided a larger set of acidity constants for this mineral. However, the $\Delta p K_a$ step cannot be reduced indefinitely to obtain a continuous distribution of acidic or basic components, as it significantly increases the calculation error, and the variation of results becomes no longer significant [41]. In our case, at a $\Delta p K_a$ of 0.25, noise in the data made it impossible to identify specific groups on the surface (Figure 2c). As soils are more complex compared to kaolinite, a $\Delta p K_a$ of 0.5 was used for this point on.

3.5. Soil Titration

For model solutions and even kaolinite, we mostly used individual pK_a values. However, for soils, it is more expedient to consider pK_a ranges because in real soils no group can be described by a single pK_a value due to intergroup interactions [2]. According to the state-of-the-art concepts, characteristic pH ranges can be distinguished (Table 4). Previously, pK_a spectroscopy has been successfully used to study the acid–base properties of humic [72] and fulvic acids [73], γ -Al₂O₃ suspensions [74], benthal sediments [75,76], and aqueous soil extracts [29]. A study was conducted on the determination of the pK_a spectra of mineral horizons of acid soils of the Republic of Komi [77], which identified four to five groups involved in protolytic equilibria, forming acid–base centers at the solid-phase surface of soils. In this study, the method of equilibrium potentiometric titration was used, and the correlation coefficients between physical and chemical parameters (exchange and non-exchange acidity, C_{org}) and pK_a were found.

pH Range	Main Determining Factors				
4.0-5.0	Reactions of carboxyl groups and H-acids of humic substances [78]				
5.0-6.5	Hydrolysis of exchangeable Al [79,80]				
6.0–7.0	HCO_3^- , CO_2 from air/water; deprotonation of carboxyl groups of water-soluble organic matter; amorphous aluminosilicates [81,82]				
8.0-8.5	Amino groups [83] and polymeric hydroxy compounds of Al [14]				
8.5–9.5	Weak OH groups of soluble phenolic, polyphenolic compounds and their hydrolysis products [83], phospholipids and diesters [84]				
9.5–10.0	Al and Fe complex compounds with organic ligands and phenolic compounds [85]				

Table 4. Main reactions in soils at different pHs according to the existing data.

3.5.1. Retisol I, Intercrown (Open) Space

To obtain the titration curves for the R I soil samples (Figure S4, Supporting Information), 10 to 25 mL of titrant was taken, depending on the horizon. Figure 3a shows the total distribution of protolytic groups, which may indicate a low humification degree of organic matter. This can be indirectly determined by the C/N ratio: in the upper horizons of this soil, C/N reaches 30, while in the lower horizons it decreases to 5–6. Low values of the indicator indicate the prevailing processes of mineralization of newly arriving organic matter, while high values indicate a slowdown in the decomposition processes in the conditions of boreal forests. At a C/N below 6, humic acids prevail; otherwise, fulvic and labile organic matter predominate. Previously, a high diversity of hydroxy acids was noted in the composition of the litter of podzolic soils in this region [86], which indicates a large number of diverse functional groups, associated mainly with aromatic acids with a wide range of p K_a values, from 5 to 10 in the upper part of the profile and from 8 to 10 in the lower part. In general, the distribution of groups also corresponds to the amounts of oxalate-soluble forms of Fe and Al.

The eluvial horizon E1 shows an expected decrease in the number of protolytic groups. Thus, the concentrations of the groups with pK_a values of 5.0, 6.5, and 8.0 sharply decrease due to the removal of the active material in the lower horizons; this is implemented with appearance of groups with pK_a 5.5, 6.0, 8.0, and 9.0. The next horizon, Eh, is characterized by humus–ferrous films on the surface of mineral grains (i.e., non-silicate forms of sesquioxides and humic substances) and high contents of groups with pK_a values of 5.0, 5.5, 6.5, 7.0, 8.0, 8.5, 9.0, and 9.5 (Figure 4a).

The distribution of protolytic functional groups along the soil profile reflects the characteristics of the substance of its genetic horizons. Thus, a high content of components with a pK_a value of 9.5 in Eh was noted in the composition of the humified ferruginous eluvial–illuvial horizon. The content of more mobile components with a pK_a value of 5.5 in the middle part of the profile is higher than that in the topsoil. This is associated with the migration of easily mobile oxalate-soluble aluminum and iron (Table 1 and Figure 5a). The crystallized species of iron oxides and phosphate compounds with a pK_a value of



Figure 3. Molar distribution of total protolytic functional groups (FG) in profiles of (a) Retisol I and (b) Retisol II. Standard deviation was calculated by 4 replicates.



rial type, with their accumulation in the n the lower part of the whole profile.



Figure 4. Molar distribution of protolytic functional groups (FG) of different strengths in mineral horizons of profiles of (**a**) Retisol I (RI) and (**b**) Retisol II (RII).



Figure 5. Distribution depth profiles of elements in (a) RI and (b) RII; ox, oxalate-soluble.

3.5.2. Retisol II (Under the Crown of Spruce)

The titration of suspensions of this soil type required 10 mL of the titrant for all horizons (Figure S5, Supplementary Information). The distributions of Fe, Al, and P in the profile are shown in Figure 5b. The physicochemical properties of R II are presented in Table 2. The distribution of acidic components is eluvial–illuvial, with accumulation in the middle part of the profile in the iron-rich transitional horizon (Figure 3b). This is due to the predominance of weak groups with pK_a values of 8.5–10.0 (OH groups of dissolved phenols, polyphenols, and their hydrolysis products, hydroxy–organic complexes of Al and Fe, Table 4). Their contents decrease down the profile and are practically aligned in illuvial, texturally differentiated horizons (Figure 4b).

The distribution of stronger carboxyl groups (p K_a 4.0–4.5) is accumulative, with the most accumulation in the upper eluvial horizon. The illuvial accumulation of groups with p K_a values of 5.0–5.5 down the profile corresponds to the vertical distribution of oxalate-soluble aluminum. In contrast to the R I soil, the distribution of acidity groups along the profile is more uniform in the R II soil, which we associate with a heavier particle size distribution, causing the formation of a pronounced soil particle structure, and less intense vertical migration of the mobile organic, organomineral, and amorphous mineral compounds. Hydrolytic (pH-dependent) acidity is associated with soil components that exhibit the properties of weak acids in general, i.e., not only exchange ions, but also components associated with varying surface charges.

Retisol II is distinguished by a high content of phenolic groups, which is typical for spruce secretions [87] and Fe and Al (columns with pK_a 10.0, 8.5 and 5.0). This is due to the chemical composition of the aqueous solutions reaching the soil surface [88]. Thus, Robakidze, Torlopova, and Bobkova [57] showed that in the waters in tree crowns, the concentration of dissolved carbon, iron, and aluminum is significantly higher.

3.6. Principal Component Analysis and Classification

Each of the studied samples was described using more than 35 factors in total (Tables 1 and 2 and Section 2.3), among which 11 are related to the content of groups with pK_a values from the titration curves: 5.0; 6.5; 8.5; 9.0; and 10.0; or ranges 4.0–6.0; 6.5–8.5; 9.0–10.0; 4.0–5.0; 5.5–6.5; and 7.5–8.5. As the number of variables is large, the principal component method was used [89–91]. The second reason for PCA application is that it provides a complex view on the properties of soil horizons. In fact, the contents of groups with given pK_a values are already the representative parameters, which can be used to study soils (as discussed in the Introduction), but PCA makes it possible to take into account each of these parameters along with others, as well as with conventional soil parameters such as the chemical composition.

Each horizon of two tested soils is described by two principal components: PC1 and PC2 (Table S1, Supplementary Information). It is possible to identify separate regions corresponding to the horizons of R I and R II soils (Figure 6). Therefore, the PCA sample is representative, and the data obtained are enough for an adequate description of the horizons. The Eh horizon of R I falls into the region corresponding to R II, as the properties of this horizon are close to the properties of the E and Eh, c R II horizons. The loading values are summed up in Table S3 (Supplementary Information). The loading diagram is shown in Figure 7. It reflects the known relationships between the properties of soil horizons: strong positive correlations between the total C and N, Al_2O_3 , and Fe_2O_3 , and negative correlation with exchangeable Ca and Mg [89,92–94]. There is also a positive correlation between the number of main groups and hydrolytic acidity (p K_a 4.0–5.0, 7.5–8.5, and 10.0). It is also clear that the contents of exchangeable calcium and magnesium are associated with the degree of saturation with bases and the pH values of both aqueous and saline solutions (to a lesser extent).



Figure 6. Principal component values: each point represents a horizon; red points are for Retisol I, and blue for Retisol II.







Figure 7. Loading values; each point represents one variable; ex, exchangeable; ox, oxalate-soluble; and dit, dithionite-soluble. Each point corresponds to a variable, and its coordinates are loadings on PC1 and PC2.

The contents of carbon and nitrogen are associated with a pK_a value of 6.5, and the content of sulfur oxide as sulfur is mainly of organic origin in these soils. The C/N ratio, which is an indicator of the humification of soil organic matter, is associated with pK_a 9.0–10.0 and, to a lesser extent, with pK_a values of 6.5–8.5 and 4.0–6.0. A pK_a value of 8.5 is virtually identical to oxalate-soluble alumina, while oxalate-soluble iron oxide is associated with a wide pK_a range from 4.0 to 8.5. The correct reflection of these known dependences confirms the correctness of the model. Thus, it can be used to search for new dependences, related to the content of protolytic groups.

It should be noted that positive or negative correlations expected from the loadings plot might be strong or weak as well, or there might be no correlation at all. Thus, we examined all the pairs of the variables for which correlation is expected.

3.7. Correlation of pK_a and Soil Indicators

As expected, the single values of pK_a did not provide much data, and more information can be mined from pK_a ranges (Table 5). This made it possible to indicate which of the conventional soil parameters are responsible for the formation of pK_a spectra for soils of the same type but developed under different vegetation.

The two studied soils differ in the degree of correlation between the carbon and nitrogen content and pK_a . In the R I soil, formed under the influence of diverse herbaceous vegetation in the intercrown space, correlations with the content of C and N were found, as well as with the degree of humification of C/N for almost all individual pK_a values (except for a pK_a value of 10, where there is no correlation, and for pK_a values of 5.5–6.5, where the correlation is medium and weak). Despite the fact that soil organic matter accumulates in the composition of plant litter in the upper thin layer, the diversity of its composition and the presence of a significant amount of aliphatic compounds provides its mobility for migration along the profile [95,96]. In the R II soil, however, we found correlations between soil carbon and nitrogen with pK_a values of 6.5 and 10 only. This soil is developed in the canopy space of spruce; in fact, it was formed under the influence of litter of a constant and homogeneous composition, in the absence of species diversity, mainly under the influence of polyphenolic compounds and their functional groups.

pK _a or pK _a Range	R I Correlation	R II Correlation	R I + R II		
5.0	Strong positive correlations with the amount of C, N, C/N, oxalate-soluble Al ₂ O ₃ and Fe ₂ O ₃ , dithionite-soluble Fe ₂ O ₃ and SO ₃	Positive correlations with the amount of oxalate-soluble Al ₂ O ₃ and dithionite-soluble Fe ₂ O ₃ . Negative correlation with C, N, C/N	Weak correlations with the amount of C, N. Correlations with the amounts of oxalate-soluble Al ₂ O ₃ , Fe ₂ O ₃		
6.5	Strong positive correlations with the amount of C, N, C/N, oxalate-soluble Al ₂ O ₃ and Fe ₂ O ₃ , dithionite-soluble Fe ₂ O ₃ and SO ₃	Strong positive correlations with the amount of C and N; negative correlation with oxalate-soluble Al ₂ O ₃ and Fe ₂ O ₃ and dithionite-soluble Fe ₂ O ₃	Correlations with the amount of C, N. Correlations with the amounts of oxalate-soluble Fe_2O_3		
8.5	Positive correlations with the amount of C, N, C/N, oxalate-soluble Al_2O_3 and Fe_2O_3 , dithionite-soluble Fe_2O_3 and SO_3	Positive correlations with the amounts of oxalate-soluble Al_2O_3 , Fe_2O_3	Correlations with the amounts of oxalate-soluble Al ₂ O ₃		
9.0	Weak correlations with the amount of C, N, C/N, oxalate-soluble Al ₂ O ₃ and Fe ₂ O ₃ , dithionite-soluble Fe ₂ O ₃	No correlations with the amount of C, N; correlation with the amount of CaO and dithionite-soluble Fe ₂ O ₃	No correlations		
10.0	Negative correlations oxalate-soluble Al ₂ O ₃ and Fe ₂ O ₃ and dithionite-soluble Fe ₂ O ₃	Positive correlations with C, N, C/N, Al ₂ O ₃ and Fe ₂ O ₃ , P ₂ O ₅ and hydrolytic acidity	Correlations with the amounts of oxalate-soluble Al ₂ O ₃ , P ₂ O ₅		
4.0-6.0	Correlations with the amount of C, N, oxalate-soluble Al_2O_3 and Fe_2O_3	Negative correlations with CaO, weak correlation with oxalate-soluble Al ₂ O ₃ , P ₂ O ₅	$\begin{array}{c} \text{Correlations with the amount of} \\ \text{C, N. Correlations with the} \\ \text{amounts of oxalate-soluble Al}_2\text{O}_3, \\ \text{Fe}_2\text{O}_3, \text{P}_2\text{O}_5 \end{array}$		
6.5–8.5	Correlations with the amount of C, N, oxalate-soluble Al_2O_3 and Fe_2O_3 and SO_3	Negative correlations with exchangeable CaO and MgO, positive correlation with oxalate-soluble Al ₂ O ₃ and Fe ₂ O ₃ and dithionite-soluble Fe ₂ O ₃ , P_2O_5	Correlations with the amount of C, N. Correlations with the amounts of oxalate-soluble Al_2O_3 , Fe_2O_3 , P_2O_5		
4.0–5.0	Correlations with the amount of C, N, oxalate-soluble Al_2O_3 and Fe_2O_3 and SO_3	Positive correlation with the hydrolytic acidity and with oxalate-soluble Al ₂ O ₃	Weak correlations with the amount of C, N. Correlations with the amounts of oxalate-soluble Al_2O_3		
5.5–6.5	Weak correlations with the amount of C, N, oxalate-soluble Al ₂ O ₃ and Fe ₂ O ₃ and SO ₃	Weak positive correlation with C, N, negative correlation with oxalate-soluble Al ₂ O ₃ and Fe ₂ O ₃ and dithionite-soluble Fe ₂ O ₃	No correlations		
7.5–8.5	Correlations with the amount of C, N, oxalate-soluble Al_2O_3 and Fe_2O_3 and SO_3	Correlation with oxalate-soluble Al_2O_3 , P_2O_5	Weak correlations with the amount of C, N. Correlations with the amounts of oxalate-soluble Al ₂ O ₃ , Fe ₂ O ₃ , P ₂ O ₅		
9.0–10.0	Correlations with the amount of C, N, oxalate-soluble Al_2O_3 and Fe_2O_3 and SO_3	Positive correlation with C, N, C/N, P ₂ O ₅ , Al ₂ O ₃ and Fe ₂ O ₃ and hydrolytic acidity	Correlations with the amount of C, N, oxalate-soluble Al_2O_3 and Fe_2O_3		

Table 5. Correlation between pK_a spectra and other soil parameters.

More correlations are found for oxalate-soluble Al_2O_3 and Fe_2O_3 . The first has a negative correlation with pK_a values of 5.0–6.5, 5.5–6.5, and 8.5. This confirms the existing data: the hydrolysis of exchangeable aluminum and polymeric hydroxy complexes of aluminum occur at pH 6.5 [79,80] and 8.5 [14], respectively. The content of oxalate-soluble Fe_2O_3 has correlations with pK_a ranges of 4.0–6.0; 6.5–8.5; and 7.5–8.5, but the strongest

one takes place with pK_a 9.0–10.0. This result fits well with the hydrolysis of Fe complexes with organic ligands at pH 9.5–10.0 [85].

In addition to sulfur, which strongly correlates with the content and composition of organic matter (carbon, nitrogen, and their ratio), only phosphorus compounds reveal acidic properties in the studied soils. The P_2O_5 content has positive correlations with pK_a values of 4.0–6.0 and 6.5–8.5, which should be attributed to the first two acidic constants of phosphoric acid [97]. In addition, no correlations of phosphorus with organic species should be expected because the acidity of such type of soils does not depend on the content of organic substances, as mentioned above. The acidity ranges 4.0–5.0 and 5.5–6.5 provided no useful information because the amounts of these groups were low.

4. Conclusions

In conclusion, potentiometric spectrotitrimetry at a fast high-resolution mode was applied to find the detailed quantitative distribution of surface protolytic groups in primary soil particles, and the results are directly connected with the soil chemical composition. Due to the high resolution, the error of assessing acidity constants from titration curves is decreased to 3–5% compared to commonly used titrimetry approaches. It is valuable that the approach provides the complete set of major acidity values (pK_a spectra) without a priori information on a soil sample. The obtained pK_a spectra can be used to distinguish the soils with matching properties and, thus, can be used to identify soils that coincide in properties and genesis but develop under the influence of different types of vegetation.

The shortcoming of this approach is that one has to choose the range of calculated pK_a spectra and the step of pK_a values, but this does not impose serious difficulties for soil titration because the soil acidic components do not require the precise values of the dissociation constants, but rather acidity range descriptors. Due to the fact that the organic matter entering the soil is always characterized by a high complexity of the composition of compounds, we recommend the analysis of the following pK_a values: 4.0–5.0; 4.0–6.0; 5.5–6.5; 6.5–8.5; 7.5–8.5; and 9.0–10.0.

The information about the amounts of the protolytic groups in Retisol soil horizons was treated in two ways. Firstly, the technique allowed us to find that the pK_a spectra do depend on the soil chemical composition for both soil types and enabled us to find the differences in the quantitative and qualitative distribution of protolytic groups of different strength both within each soil profile and between the two Retisols under different plant covers. Secondly, the results of the correlation analyses agree with the known soil chemistry and with the distribution of the protolytic groups through the horizons. This feature may be of value for screening and identification applications. We believe that fast high-resolution pK_a spectrotitrimetry, guided by chemometric approaches, can be used for various agrochemical, environmental, and genetic studies of acidic soil and soil horizons.

Supplementary Materials: The following supporting information can be downloaded at: https: //www.mdpi.com/article/10.3390/soilsystems8020063/s1, Figure S1: The location of the soil profiles: $61^{\circ}45'43.4''$ N $54^{\circ}17'50.3''$ E. Figure S2: Titration of acid mixtures with 0.1 NaOH. Explanations are in the text. Figure S3: Titration curves of kaolinite. Figure S4: Titration curves of Retisol I. Figure S5: Titration curves of Retisol II. Figure S6: Correlation coefficients between indicators of acid properties, general physicochemical characteristics of soils and pK_a . Table S1: Principal component values for the PCA analysis of soil horizons. Table S2: Bulk content of main elements in soils. Table S3: Loading values for PCA analysis of soil.

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