

Fig. 1. Basic design (schematic) of instrument for determining soil-water potential.

porous block in hydraulic contact with the soil. We propose a new principle of measurement that promises improved accuracy over the full range of soil-water potentials that is of practical interest in agricultural and other problems.

The specific free energy of water in an aqueous solution is lower than that of pure water under the same conditions, but by application of pressure to the solution the specific free energy of the water can be restored to its value in the pure state. The pressure required to effect restoration is defined as the osmotic pressure of the solution. If pressure less than the osmotic pressure is applied, the specific free energy of the water is increased to a value intermediate between that in the solution and that of pure water.

Thus the addition of a solute provides a convenient means of depressing the specific free energy of water below the standard reference level; with sufficient depression, the specific free energy of water in an aqueous solution can be made less than that in a particular soil.

Let us consider an isothermal system consisting of such a solution physically constrained in a container that is surrounded by unsaturated soil; it is so arranged that water, but not solute, can be exchanged between solution and soil. Water will move from soil to solution, increasing the pressure of the solution until at equilibrium the specific free energy of water is the same throughout the system. In centimeter-gram-second units, the difference between the equilibrium pressure and the osmotic pressure of the solution is numerically equal to the specific free energy of the soil water (4); this difference is also a measure of the potential of the soil water. The determination of soil-water potential then reduces to simple measurements of pressures in excess of atmospheric.

In order to apply this principle we are constructing instruments basically similar to the classical osmometer (Fig.

1). So long as a specific free-energy difference exists between the water in the soil and that in the solution, water moves through the semipermeable membrane and its porous support with consequent changes in solution pressure.

A basic factor in design is the quantity of water that must pass through the semipermeable membrane to bring about unit change in solution pressure. This factor must be kept as small as possible in order to minimize (i) change of solution concentration; (ii) soil-water disturbances; and (iii) the time constant of the instrument, which is determined by this factor and by the resistance of the semipermeable membrane and its porous support to water transfer.

A suitable membrane-solute combination appears to be Visking dialysis membrane and polyethylene glycol of molecular weight 20,000 (5), but other combinations may prove to be preferable. We have used commercial pressure transducers and others of our own construction. It is generally desirable that the support plate should be finely porous, as water transfer through the plate should be in the liquid phase. In the absence of liquid transfer through the plate, equilibration will be by way of the vapor phase, and in general the instrument's time constant will be increased significantly.

Commonly the soil water will contain solute molecules (different from the basic solute within the instrument) that can pass through the semipermeable membrane. In such instances the instrument indicates not the total water potential but what is now commonly called the matric potential (3, p. 14). The instrument can be adapted to measure the total water potential in the presence of soil-water solutes by the deliberate inclusion of a vapor gap within the porous support.

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Precipitate Formation in the Strontium-Phosphate System

Abstract. Study of the precipitation process in the aqueous $\text{Sr}(\text{OH})_2\text{-H}_3\text{PO}_4$ system, in order to elucidate the phase transformations and the nature of the final solid phases, shows that over much of the range of compositions studied the initial precipitate is poorly crystalline; the x-ray pattern resembles that of strontium hydroxyapatite but has a strontium:phosphorus molar ratio close to 1.3. Within 1 hour the initial precipitate changes to a stable crystalline phase (or phases), with corresponding change, either up or down, in the strontium:phosphorus ratio. At high ratios of $\text{Sr}(\text{OH})_2$ to H_3PO_4 the initial precipitate is $\text{Sr}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$, which then converts to a phase having the x-ray diffraction pattern of strontium hydroxyapatite, but having a strontium:phosphorus ratio that depends somewhat on the initial ratio of $\text{Sr}(\text{OH})_2$ to H_3PO_4 used in the precipitation.

In studying the titration curve of strontium hydroxide versus phosphoric acid at 38°C, Holt, Pierce, and Kajdi (1) found that, when less than one equivalent of strontium hydroxide was added, the curve of pH versus amount of $\text{Sr}(\text{OH})_2$ was the normal acid-base titration curve; but when more than one equivalent was added precipitation occurred. The curve of pH versus equivalents of strontium hydroxide showed one plateau just beyond one equivalent, another between two and three equivalents. The molar ratio of Sr:P in the solid changed from 1.0 at one equivalent to 1.53 at three equivalents of strontium hydroxide.

Their characterization of the solid phase was based on only chemical and microscopic analyses and their understanding of the nature of the various precipitates was consequently incomplete. When two new strontium phosphate phases were discovered (2), I tried to clarify the relation between the various solid phases by systematically investigating the $\text{Sr}(\text{OH})_2\text{-H}_3\text{PO}_4$ titration curve, with x-ray diffraction analyses of the solids.

The titration data were obtained by the method of Holt *et al.* (1). Various amounts of $\text{Sr}(\text{OH})_2$ were added to 100-ml solutions containing 0.002 equivalents of H_3PO_4 ; each solution was diluted to 200 ml and each reaction flask was sealed and placed on a shaker. One series of experiments was carried out at $24^\circ \pm 1^\circ\text{C}$ (except for a rise to

28°C in the middle of the run) for 30 days; the other series, at $38^\circ \pm 1^\circ\text{C}$ for 21 days. At the end of the equilibration period the pH of the solution was measured and the solid phase was filtered off, washed slightly, and air dried at room temperature; its x-ray diffraction pattern was recorded and its Sr:P ratio was determined.

The molar ratio Sr:P in the solids was determined by means of x-ray diffraction analysis of samples that had been heated to 950°C ; at this temperature all strontium phosphates in the range studied are converted to mixtures of $\alpha\text{-Sr}_2\text{P}_2\text{O}_7$ and $\text{Sr}_3(\text{PO}_4)_2$, or $\text{Sr}_3(\text{PO}_4)_2$ and $\text{Sr}_{10}(\text{PO}_4)_6(\text{OH})_2$. Since these three components appear to be stoichiometric compounds, the relative amounts of these phases are uniquely determined by the Sr:P ratio in the original sample. By determination of the relative intensities of x-ray diffraction lines characteristic of each phase, and by comparison of these with similar measurements from synthetic mixtures of the components, the Sr:P ratio in the sample can be calculated. Intensity measurements were made on powders sieved through 325 mesh; a diffractometer was employed, with proportional counter detector and strip-chart output. Large errors in Sr:P ratio may arise by this method if the compounds are nonstoichiometric. With Sr:P ratios lower than 1.50 errors are less than ± 0.02 , since, for pure $\text{Sr}_6\text{H}_3(\text{PO}_4)_5 \cdot 2\text{H}_2\text{O}$ and $\text{Sr}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$, chemical analyses and the x-ray method agree to within this figure. Unfortunately no chemical analyses are available for comparison on samples with Sr:P ratios exceeding 1.50, and the possibility cannot be definitely excluded that an error larger than ± 0.02 may exist in this region, although the standard strontium hydroxyapatite sample heated to 950°C showed no extraneous x-ray diffraction lines.

For up to 10 or 15 minutes after the strontium hydroxide and phosphoric acid solutions are mixed together the turbidity is low, but it then increases strikingly. The changing nature of the solid phase with time was studied by rapid filtration of the solid from its mother liquor; the solid was dried by pressing between filter papers, and an x-ray diffraction pattern from the damp sample was made with a proportional counter diffractometer. The Sr:P ratios were also measured from these rapidly isolated precipitates by the method described above, but, since no effort was made to remove all traces of solution

and since many of these precipitates are gelatinous, the ratios may be somewhat in error because of occluded solution.

The titration curves in the equilibration experiments, pH versus equivalents of $\text{Sr}(\text{OH})_2$ added, are shown in Fig. 1 for 24°C and 38°C ; the nature of the final solid phases and their molar Sr:P ratios are also indicated. Table 1 shows both the phase and Sr:P ratio analyses for samples isolated at various times after precipitation had started, for various starting compositions ranging in additions from 1.6 to 3.2 equivalents of $\text{Sr}(\text{OH})_2$. Clearly the precipitate changes with time.

For convenience in the discussion, the range of compositions studied can be divided into two parts (see Fig. 1): solutions in which the amount of $\text{Sr}(\text{OH})_2$ added is more than sufficient to neutralize 2.6 equivalents of H_3PO_4 ; and solutions in which 2.6 or less equivalents are neutralized. In the former region the initial phase that forms contains $\text{Sr}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ (2); this phase gradually transforms into a phase having an x-ray diffraction pattern characteristic of strontium hydroxyapatite if it is left in contact with the mother liquor; in boiling solutions the change is exceedingly fast and $\text{Sr}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ cannot be isolated. At temperatures close to 0°C the latter phase is stable for many days. At 24°C and 38°C the transformation to the hydroxyapatite structure is complete at least within the

Table 1. Change in composition of solid phase with time at 24°C . A, Amorphous.

Added equivalents of $\text{Sr}(\text{OH})_2$	Sampling time after precipitation (min)	Solid phase	Sr:P in solid
1.6	6	A	1.27
1.6	15	A + SrHPO_4	1.13
1.6	28	SrHPO_4	1.00
1.8	0	A	
2.0	0	A	
2.2	0	A	1.32
2.3	0	A	1.33
2.3	4	A + $\text{Sr}_6\text{H}_3(\text{PO}_4)_5 \cdot 2\text{H}_2\text{O}$	1.29
2.3	8	A + $\text{Sr}_6\text{H}_3(\text{PO}_4)_5 \cdot 2\text{H}_2\text{O}$	1.25
2.3	15	$\text{Sr}_6\text{H}_3(\text{PO}_4)_5 \cdot 2\text{H}_2\text{O}$	1.22
2.4	0	A	1.33
2.4	30	A + $\text{Sr}_6\text{H}_3(\text{PO}_4)_5 \cdot 2\text{H}_2\text{O}$	1.24
2.6	0	A	1.37
2.8	0	A + $\text{Sr}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$	1.44
2.8	30	A + $\text{Sr}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$	1.47
3.2	0	$\text{Sr}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$	1.50

30 and 21 days, respectively, that were used for the titration experiments, but, as can be seen in Fig. 1, the Sr:P ratio of this phase varies from 1.50 to 1.67 (the theoretical value for strontium hydroxyapatite), depending on the starting composition of the system. The x-ray diffraction pattern is not as sharp as that from highly crystalline strontium hydroxyapatite (for example, a sample prepared at high temperatures), and the variable Sr:P ratio may reflect either phosphate adsorption on the surface of small particles or a disordered defect structure.

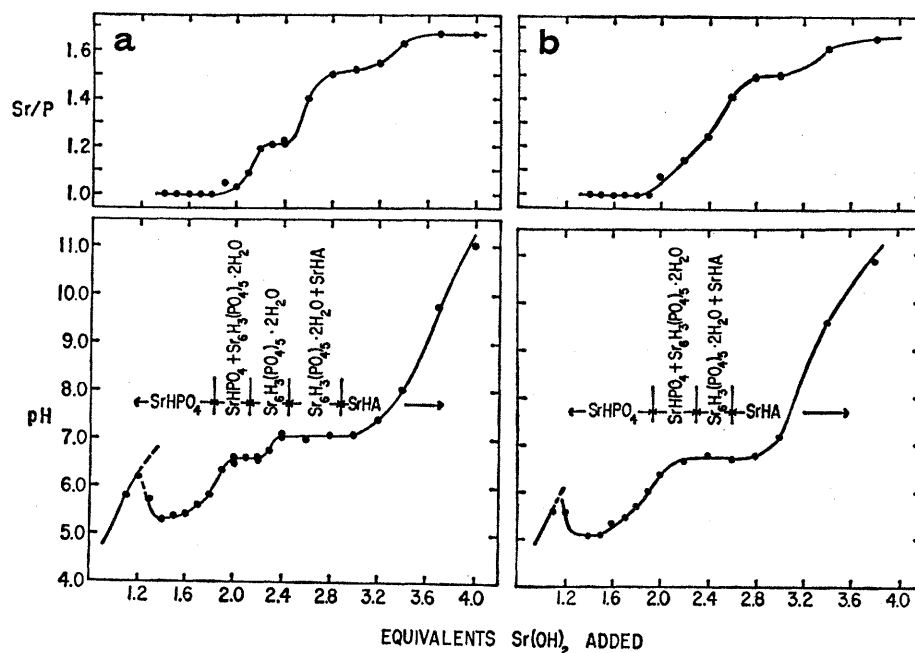


Fig. 1. Titration curves of $\text{Sr}(\text{OH})_2$ against H_3PO_4 : a, at 24°C ; b, at 38°C . The lower curves show the variation of pH with various added equivalents of $\text{Sr}(\text{OH})_2$, as well as the nature of the solid phases present. The upper curves give the Sr:P ratio of the solid phases.

For the other range of compositions, additions of less than 2.6 equivalents of $\text{Sr}(\text{OH})_2$, $\text{Sr}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ is not observed in even the earliest precipitates than can be isolated. Instead, the first precipitate has a diffuse x-ray pattern and hence is called an amorphous phase; it has a remarkably constant Sr:P ratio close to 1.3 for a wide range of starting compositions—from 2.6 to 1.6 equivalents of $\text{Sr}(\text{OH})_2$; its diffraction pattern exhibits a strong line at $d = 2.91 \text{ \AA}$ and a weaker line at $d = 3.63 \text{ \AA}$ superimposed on a very broad reflection between 4.4 and 2.6 $\text{\AA}$. The stronger line corresponds to the strongest line of the strontium hydroxyapatite pattern and may indicate structural similarity to this material. Interestingly, the Sr:P ratio of this phase is close to the Ca:P ratio in octacalcium phosphate (3).

The amorphous phase precipitates very shortly after the solutions are mixed. Composition of the precipitate then starts changing rapidly toward its final nature (see Table 1), which is reached within 30 to 60 minutes of the earliest precipitation.

The titration curve at 38°C (Fig. 1b) generally agrees with that of Holt *et al.* (1) apart from the dip in pH at 1.4 equivalents of $\text{Sr}(\text{OH})_2$, which they did not observe; in this region the precipitation occurs very slowly and, since the total amount of precipitate formed is small, the nature and composition of the initial phase was not determined. In the region below 1.8 equivalents of $\text{Sr}(\text{OH})_2$ the final precipitate is a mixture of α - and β - SrHPO_4 in the experiments at 38°C , but only β - SrHPO_4 at 24°C .

Holt *et al.* (1) have suggested that the observed increase in Sr:P ratio at between 2.0 and 2.8 equivalents of $\text{Sr}(\text{OH})_2$ may be caused by adsorption of strontium ions on the surface of SrHPO_4 crystals. It is apparent from the x-ray diffraction analysis that this hypothesis is unlikely and that the increasing Sr:P ratio in this region is merely a consequence of the changing amounts of the three compounds SrHPO_4 , $\text{Sr}_6\text{H}_8(\text{PO}_4)_5 \cdot 2\text{H}_2\text{O}$, and strontium hydroxyapatite. This point is most clearly illustrated in Fig. 1a, where a plateau occurs on the Sr:P curve at about 2.3 equivalents and corresponds to the formation of a single compound.

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Fluctuations of Resting Neural Membrane Potential

Abstract. *The membrane potential of myelinated axons in the resting state shows fluctuations for which the power per cycle of bandwidth is inversely proportional to frequency between 1 and 10,000 radians per second. Reduction of potassium ion flux leads to a decrease in noise power.*

Statistical analyses of action potential time series recorded from neural elements have furnished important data on spontaneous and induced neuronal activity, and several models have been proposed to explain them. In most models, one or more random processes are invoked. In one aspect, however, the models are arbitrary, for experimental evidence on random processes in neural elements is lacking.

One such process, thermal noise, has been invoked by some neurophysiologists to explain irregular neuronal activity. By thermodynamical arguments, Nyquist has shown (1) that the minimum intensity of the noise voltage in an electrical conductor is given by $N = e^2 = 4kTR$, where N (in volt² sec) is the noise power per cycle of bandwidth, e is the open-loop voltage over the resistance R , k is Boltzmann's constant, and T is absolute temperature. When the resistance is independent of frequency the Nyquist noise power is also independent of frequency ("white" noise). Additional sources of noise are possible—for example, in semiconductors.

Fatt and Katz suggested (2) that thermal noise across the resistances of membrane and core of axonal endings might be the cause of spontaneously occurring miniature end-plate potentials. Buller *et al.* (3), Hagiwara (4), and Buller (5) considered the possibility that thermal noise might account for the spontaneous activity of frog

muscle spindles and for the irregularities in their discharge under stretch. Hagiwara, however, doubted that the intensity of noise from this source was high enough to explain these phenomena.

Fluctuations in excitability of axons and in the latencies of their responses, first described by Blair and Erlanger (6), and investigated by Pecher (7), were extensively studied by Verveen and co-workers. The statistical properties of these fluctuations (8, 9) could be explained by assuming the existence of a noise voltage over the resting axon membrane (9, 10), with a root-mean-square value on the order of a millivolt for myelinated axons of small diameter and with smaller values for larger axons (11).

Thermal noise, according to Nyquist's theorem, is, however, insufficient to account for these phenomena (compare figure 2 in Verveen, 11). It was, therefore, necessary to acquire direct information on fluctuations in the potential of resting membranes (membrane noise voltage). Because of the influence of membrane noise voltage on signal transmission and data processing in the nervous system, the receptor cell membrane, the presynaptic membrane, the dendritic membrane, and the initial axon segment would be the objects of choice, but technical difficulties preclude this approach at present. This leaves the axon membrane as the object for initial investigations.

Measurements on a nodal membrane—internodal axoplasm—nodal membrane system were published earlier (9). With this two-terminal system it is difficult to evaluate the contribution of the membrane, both because of the necessity for correcting for the noise contributed by electrodes and amplifiers, and because of the difficulty of pinpointing the actual noise source. We now report experiments in which the noise from a single Ranvier node was measured by using a three-terminal arrangement and performing a correlation analysis on the outputs of the two two-terminal arrangements of which it consists (12, 13).

A length of frog sciatic nerve fiber containing three nodes was mounted in a tray with five pools filled with Ringer solution. The middle node lay in the central pool and each of the other nodes in one of the outer pools. The second and fourth pools were used for electronic feedback compensation of the external fluid shunts between adjacent nodes (Frankenhaeuser, 14). The poten-