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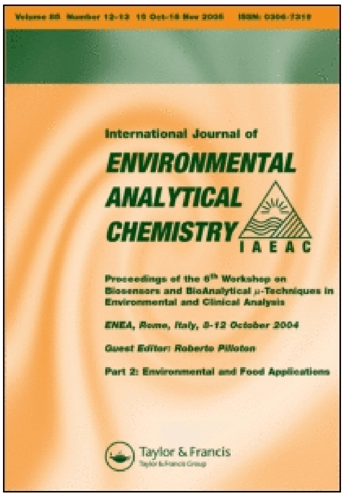

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AN ION-SELECTIVE FIELD EFFECT TRANSISTOR FOR *IN SITU* pH MONITORING OF WET DEPOSITION*

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The search for a suitable miniature electrode system for *in situ* measurements of the pH of wet deposition has led to tests with hydrogen-ion sensitive field effect transistors (pH-ISFETs).

Initial testing was done under laboratory conditions and focussed on the stability and reproducibility of the electrode response under flow conditions, firstly with buffered solutions in the pH range 4.1 to 5.0, a range typical for rainfall in this area of Switzerland, and thereafter with unbuffered solutions in the pH range 3.0 to 5.0. Emphasis was also placed on the choice of reference electrode and on the design of the flow cell for field tests. The effect of temperature on the ISFET response—with a view to eventually compensating for this parameter—could be followed by means of a diode mounted on the ISFET holder.

Based on the results of laboratory tests, operational conditions in the field were chosen. Some of the initial field results are presented, and the specific problems occurring with the field model are outlined and discussed.

KEY WORDS: ISFET, pH, *in situ* pH monitoring, rain.

INTRODUCTION

In environmental studies, pH is an important parameter describing the quality of a rain event. As such, the measurement of pH is not without its problems, particularly when being measured in solutions of low ionic strength,[1] such as rain. Measurement of this parameter is usually carried out on the bulk of the deposition, collected either on an event basis or after periods of days, weeks or months.[2,3] A minimum volume of 20 ml is often required for the analysis of all chemical components. Studies on the frequency and duration of ambient rainfall in the US indicate that the majority of the events are of relatively short duration and small volume;[4] analysing samples taken over periods of days or even weeks could obscure a diversity of characteristics that plant foliage may experience. Our long-

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term aim is to improve the information obtained from event-based measurements. This particular study is concerned with developing a system which records the changes in the pH of rain *in situ*, in a cell volume of less than 1 ml; similar studies[5] performed to date have not, as far as we know, aimed at such low volume resolution nor measured the pH under flow conditions. In this way, it is hoped that more information can be obtained about the way in which pH changes during a rain event, and in particular about the peaks or extreme values which the environment experiences. At the same time, however, it is not the intention of this study to replace pH measurements done on the bulk of the deposition.

The development of a measuring system to record the pH of wet deposition at short time intervals has several prerequisites: a reproducible response with short response times from the electrode system and a measurement cell with a small volume (under 1 ml) to reduce dilution effects on the pH as more rain falls. The additional restraints posed by field conditions mean that this system should ideally be robust, compact, and capable of operating alone and remaining stable for periods of at least one week. If this system is also relatively cheap to make, it will have the added advantage of being able to be implemented on a large scale without costs becoming prohibitive.

Many of the constraints placed on pH measurements in environmental monitoring are also relevant for electrodes employed in the field of biomedical engineering, and it is for this latter application that the solid-state ion selective field effect transistor (ISFET) has been developed.[6] ISFETs are rugged, have a small surface area (*c.* 1 mm^2) and fast response.[7] They also have low impedance and are therefore less sensitive to motion artifacts and electromagnetic interference than other potentiometric sensors, including the glass electrode. The fact they can be mass produced means they should be much cheaper than conventional electrodes. To our knowledge, this is the first attempt to use them in environmental monitoring and additional applications, such as continuous pH measurements of soil solutions, are foreseen.

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MATERIALS AND METHODS

1. Reagents

The reagents used for the preparation of the test solutions were all of analytical grade (Merck p.a.) and deionized water cleaned by additional ion exchange and filtration through activated charcoal and a 0.45 μm filter (Millipore, Milli-Q) was used throughout. Standard buffers (with pH values 4.1, 4.4, 4.7 and 5.0) were prepared from mixtures of 0.1 M potassium hydrogen phthalate and 0.1 M sodium hydroxide solutions. Unbuffered solutions with pH 3.0, 3.5 and 4.0 were prepared from an appropriate dilution of 1 M HCl (Titrosol, Merck) and the remaining unbuffered solutions (with pH values 4.5 and 5.0) from dilutions of 0.1 M HCl; in the case of the pH 5 solution, the deionized water was deaerated with N_2 prior to addition of the HCl.

2. *Electrodes*

The pH-ISFETs used in this study were developed at the "Centre Suisse d'Electronique et de Microtechnique S.A." (CSEM), Neuchatel. They were of the *n*-channel type and had an Al_2O_3 membrane as the ion-sensitive layer; the ISFET chip measured approximately 2 × 0.5 mm. The encapsulation, an important factor in determining the lifetime of the device, was done with the epoxy Epon (Shell). The working values for I_{ds} (between 50 and 100 μA) and V_{ds} (between 0.5 and 1 V) were set according to the recommendations from CSEM. For details on the theory and operation of ISFETs, see Janata and Huber.[8]

Various reference electrodes were tested in order to determine which would be most suitable for field tests. The majority of the laboratory tests were done with a calomel electrode (Philips R 11-NS) inside a sheath ending in a 3.5 mm ø Vycor frit and filled with saturated KCl. Since this electrode was felt to be too cumbersome, the reference electrode chosen for the field flow cell was a 6.5 cm long Ag/AgCl reference electrode (from the Metrohm VA-Stand 647), which had a polychlortrifluoroethylene (PCTFE) casing and was filled with 3 M KCl.

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3. *Instrumentation*

In the laboratory tests, the solutions were delivered to the flow cell by means of a perstaltic pump (Pharmacia P-3) connected to tubing of different diameters (Ismatec) to extend the flow-rate range from the pump. A control box operated the ISFETs in the feedback mode, in other words under constant drain-source current, where the change in output voltage to keep this current constant was measured. The control box was supplied by a 9-volt rechargeable battery. In the field, the diode for measuring temperature was also run from this power source.

For the field tests, the recorder was coupled to a rain sensor so that the signal from the ISFET was only measured during a rain event.

4. *Flow Cells*

Figure 1 shows a diagrammatic representation of the flow cell used for the laboratory tests. This somewhat simple structure consists of a short length of silicone tubing connected to a small funnel for the entry of the test solution under "gravitational flow", as it would enter in the field. The Vycor frit of the reference electrode assembly enters the tube through a small hole in the side.

Details of the field flow cell are given in Figure 2. The body of the cell is machined out of a block of plexiglas, with holes of appropriate size for the ISFET + diode holder (nylon tube) and reference electrode which was placed before the ISFET in the direction of flow. This position was chosen as a consequence of the results from laboratory flow-change tests; it was found that when the "rain" entered the cell approximately "parallel" to the reference electrode, the measurement system showed the least variability under conditions of different

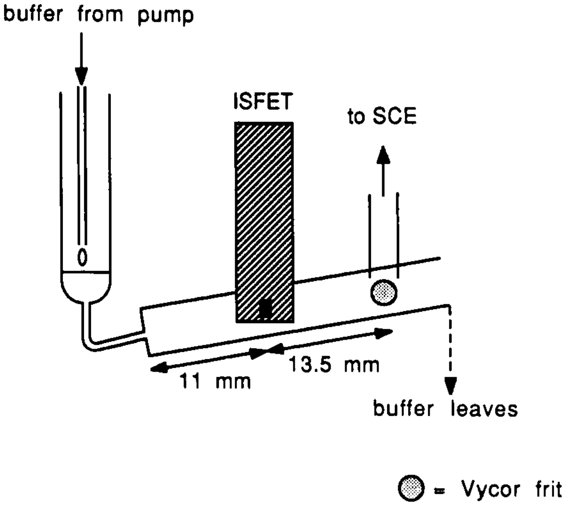

Figure 1 Diagrammatic representation of the flow cell used for laboratory tests.

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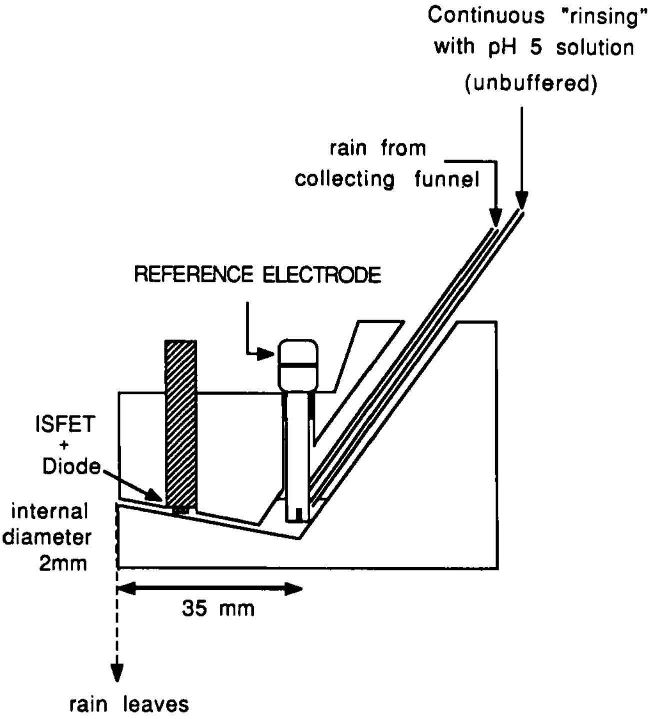

Figure 2 Diagrammatic representation of the field flow cell. The cell is mounted in a light-tight, metal box. Rain arrives at the cell from the collection funnel via a series of tubes. The purpose of the rinsing solution (pH 5) is explained in the text.

flow, but identical pH. The entry hole for the rain and the "rinsing" solution, machined at an angle for the above reason, is large enough to accommodate heavy rainfall without overflow. The rain was collected in a 25 cm ø polyethylene funnel, which remained uncovered between rain events, and led to the flow cell via a series of PVC tubes of ever-decreasing diameters. In order to reduce the drift of the ISFET to a minimum, and to prevent build-up of KCl from the reference electrode etching the Al_2O_3 gate membrane, a "rinsing" solution with pH 5 (unbuffered) and flow of approximately 0.3 ml/h was continuously siphoned to the flow cell.

The flow cell with its accompanying electronics, "rinsing" tank and collection funnel was housed in an already-existing deposition collector on the roof of our institute. Given the well-known light sensitivity of these devices, the flow cell was mounted in an additional, light-tight metal box which could also be earthed along with all the cables associated with the system to avoid electrostatic interferences.

5. *Methods*

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The main aim of the laboratory tests was to get information with regard to the following aspects:

- —the influence of flow on the stability of the response;
- —the reproducibility (within one run and from one run to the next) of the output voltage of the ISFET;
- —the pH sensitivity (mV/pH) of the ISFET over the range studied;
- —the effect of buffered versus unbuffered solutions;
- —how the ionic strength of the test solution influences the stability of the response;
- —the long-term drift associated with ISFET devices;[9]
- —the choice of reference electrode.

In addition, for field operation, measurement of the variation in the ISFET response with temperature is necessary; for this reason a diode was mounted on the ISFET holder and this enabled the simultaneous recording of a temperature signal to be made along with the ISFET output. Calibration of the diode is presently done in the laboratory. The field tests also included a study of the problematics of the collection system.

RESULTS AND DISCUSSION

1. *Laboratory Tests*

Typical plots from two ISFETs in unbuffered (a) and buffered (b) solutions under constant and identical flow conditions are shown in Figure 3. In general, no differences could be detected between buffered and unbuffered solutions; for plot

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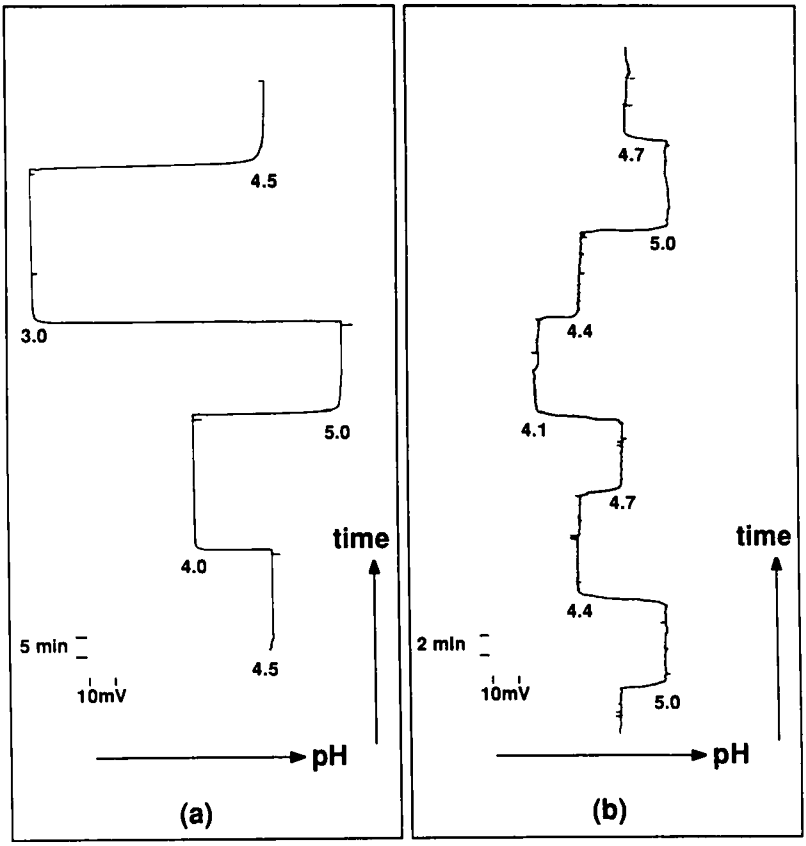

Figure 3 Outputs from two ISFETs in the laboratory flow system for (a) unbuffered (pH 3.0 to 5.0) and b) buffered (pH 4.1 to 5.0) solutions. Flow rate = 0.8 ml/min. The scales are shown in the figure.

3(a), the noticeable increase in stability is due to the fact the reference electrode was positioned vertically in the entry funnel and not in the side of the flow cell as in plot 3(b).

The corresponding plots of the ISFET pH sensitivities from these two runs can be seen in Figure 4; the values are below-Nernstian, a typical feature of these devices,[7,9] and the plots show good linearity over the range studied. In addition, the reproducibility of the ISFET responses in the flow system was always within tolerable limits (i.e., below 0.1 pH units), irrespective of whether the solution was buffered or unbuffered, and provided the flow rate was constant.

Studies on drift characteristics over long periods of time also gave satisfactory results; the drift for the first 10 hours (from dry) was always greater (in the range 0.3 to 1 mV/h) than the drift after this time (between 0.02 and 0.09 mV/h).

The major problems encountered in the flow tests appeared when the flow rates were changed, for example from "no flow" to flow conditions, or from a flow of 0.6 ml/min to 4.5 ml/min; these problems manifested themselves as differences in the absolute output voltage for a particular pH value; unbuffered pH 5.0 appeared

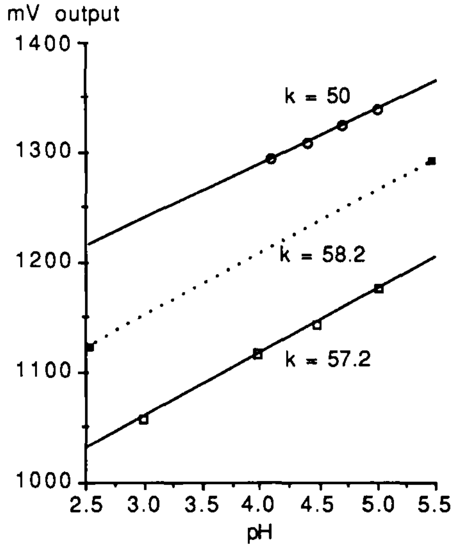

Figure 4 pH sensitivities of two ISFETs used in this study. ○: Output from ISFET in buffered solutions (V_{ds} = 1.00 V, I_{ds} = 100 μA). ■: Ideal Nernstian slope at 20°C. □: Output from ISFET in unbuffered solutions (V_{ds} = 0.50 V, I_{ds} = 50 μA).

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to be the most sensitive in this respect. Adding KCl (to a final concentration of 0.05 M) to increase the ionic strength of the unbuffered solution did not appear to improve the situation.

What did contribute to reducing the effects encountered with the flow changes came to light after a series of reference electrode tests. These tests with various reference electrodes (calomel or Ag/AgCl, different sizes, frit or sleeve liquid junctions, different positions in the flow cell, different concentrations of the KCl internal filling solution and even different flow-cell designs) showed that the major improvements on the homogeneity of the flow-cell response under different flow conditions came when the reference electrode was placed before the ISFET in the flow cell, so that it could be positioned almost parallel to the direction of flow; this is the case for the results shown in Figure 3(a). Exactly why this position should decrease the flow change effects is not exactly understood.

2. *Field Tests*

Figure 5 shows the recording of the pH of a rainfall of 225 min duration; there is no temperature compensation on this plot, and the "rinsing" solution of pH 5 was also flowing simultaneously through the cell. The signal from the rinsing solution can be clearly seen at the beginning of the recording before any rain had reached the cell. That it took nearly 20 min for the first measurement of the rain's pH to be recorded is due to the nature of the polyethylene collection funnel. Raindrops stick on the surface of the funnel and are not released to the cell until what seems like a

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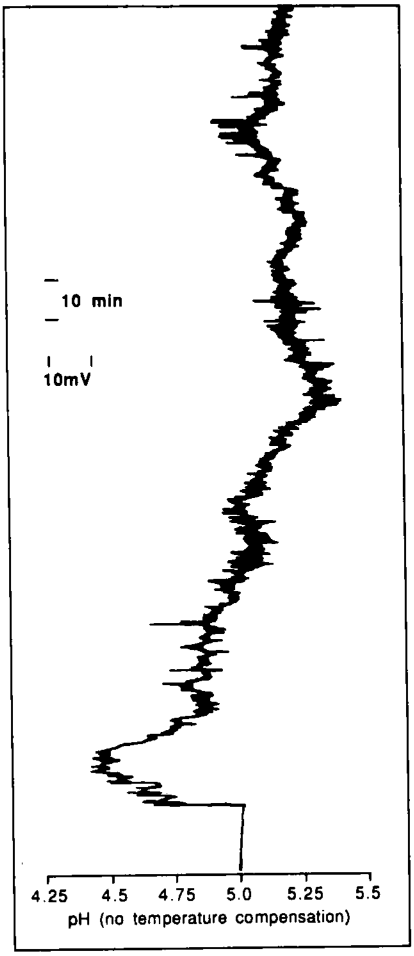

Figure 5 ISFET output showing pH changes during a 260 min rainfall (without temperature compensation and with continuous flow of the rinsing solution). The scales are given in the figure.

"critical" number are present. Not only does this delay the start of the measurement, but once measurement has started, the rain tends to arrive at the cell in "bursts" which contribute to the noise of the signal recorded. Efforts are presently being made to improve this situation.

Another factor responsible for the noise of this recorded signal is the presence of the rinsing solution. Because the rain arrives at the cell in pulse-like bursts, the time interval between bursts is long enough for the ISFET to respond to the presence of the rinsing solution. This effect is shown in Figure 6, which was recorded during an *in situ* calibration in which an unbuffered solution of pH 3 was introduced by means of a peristaltic pump (0.8 ml/min) into the collection funnel to ensure a constant flow. Because of the high paper speed on the recorder, the tendency of the signal to move towards pH 5 between the bursts of pH 3 can be clearly seen in the lower half of the figure. (Of course, the greater the difference between the pH of the rain and that of the rinsing solution, the greater the noise from this source will be.) The top half of the figure shows a much quieter signal from the pH 3 solution only, where the noise experienced is due to the pulse-like delivery of the solution to the cell. These results make it clear that the flow of the rinsing solution should be stopped during rainfall.

Although the field system is so designed that measurement of the solution in the cell only starts at the onset of rain, the continuous presence of the rinsing solution allows periodic control checks to be made between rain events. A series of such checks enabled an *in situ* study of the effect of temperature on the output voltage of the ISFET to be carried out. Some results can be seen in Figure 7 which shows the simultaneous measurement of diode voltage (and the corresponding temperature based on a calibration of the diode, which gave a slope of 2.52 mV/°C) and ISFET voltage from the pH 5 rinsing solution. The ISFET-temperature relationship can be seen to have a negative slope, but more tests need to be performed to determine if the relationship is linear over the whole pH range in question; the development of a suitable calibration procedure is under way.

Despite these "problem" areas, the first field results, exemplified by the plot in Figure 5 shows considerable promise. pH changes are visible, and especially the lower pH values at the start of the rainfall have been detected by this method. In order to start interpreting these results in any quantitative manner, additional information is required. Measurement of pH in this way only represents the "free" acid or "effective" hydrogen ion concentration in the sample. In this area of Switzerland, summer rain tends to be partially neutralized because of increased ammonia emissions from the widespread use of agricultural fertilizers.[10] It is therefore planned to incorporate simultaneous conductivity measurements into the present measurement system in order to gain information about the total ionic concentration of the deposition.

However precise and rapid the response from the ISFET is, probably the greatest source of difficulty in a pH cell still remains: the residual liquid-junction potential error.[11,12] Although efforts have been made in this study to minimize this error (e.g., similar ionic strengths of calibration and test solutions), the rinsing solution probably has a lower ionic strength than the rain, especially in summer with higher concentrations of not only ammonium but also sulfate and calcium ions.[2] The dimension of the error incurred from this source in conjunction with the ISFET has, however, not been established. Ideally, the ISFET would be combined with a compatible, miniature solid-state reference electrode, but given the present state-of-the-art this does not seem to be possible.

CONCLUSION

In terms of continuously monitoring the pH of wet deposition, the application of ISFETs lends a viable alternative to the glass electrode, with the additional advantages that the ISFET is more rugged, smaller and responds faster. The stability and reproducibility of the response in the pH range tested (3.0 to 5.0) are within well-tolerable limits especially when the reference electrode is positioned

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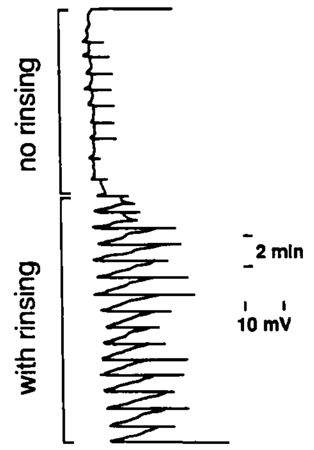

Figure 6 Influence of the rinsing solution (pH 5) on the output from the measurement of pH 3 (delivered into the collection funnel by a pump).

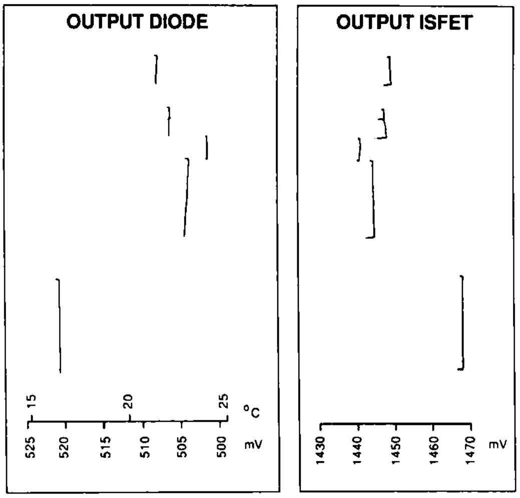

Figure 7 The simultaneous measurement of temperature (by the diode) and pH 5 (by the ISFET) showing the effect of temperature on the ISFET output voltage.

"parallel" to the direction of flow. There appears to be no difference in the stability of the response between buffered and unbuffered solutions.

Initial field tests have produced encouraging results. There is a need for temperature measurement and compensation, and on-line conductivity measurements are essential before the results can be interpreted quantitatively. Problems remain with the collection system which delivers the rain to the cell in bursts instead of at a continuous, constant flow. That a conventional reference electrode has to be used in the system means that there are still errors arising from the residual liquid junction potential. If these problems can be solved, there seems no reason to doubt that the system as it now stands could record the pH of rain continuously with reasonable accuracy.

Collaboration

The ISFETs were developed by CSEM, Neuchatel, under contract from the "Eidgenössische Anstalt für das forstliche Versuchswesen (EAFV)" (Swiss Federal Institute of Forestry Research, Birmensdorf, Switzerland). The work described in this paper was carried out in close collaboration with the soils research group of EAFV under the leadership of Dr P. Blaser.

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