REAL-TIME SOIL NITRATE SENSING

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ABSTRACT

Ion-selective field effect transistors (ISFETs) have inherent features such as small dimensions, low output impedance, high signal-to-noise ratio, low sample volumes and the potential for mass production, which are required for a real time soil sensor. However, ISFETs have the disadvantage of long-term drift, which is diminished by the use of a Flow Injection Analysis (FIA) system. In fact, FIA and ISFETs are complementary since the small sample volumes and rapid response of ISFETs allow the miniaturization of the FIA system, dramatically decreasing the sample dispersion and thereby increasing both sample resolution and sample frequency.

A multi-ISFET nitrate sensor was developed and integrated into a flow injection system to measure soil nitrates. The multi-ISFET sensor was successful in measuring soil nitrates in manual soil extracts ($r^2 > 0.9$). The precision and accuracy of the system were highly dependent on maintaining precise, repetitive injection times and maintaining constant flow parameters during the testing cycle. During tests almost all of the errors in prediction can be traced to these two factors. The rapid response of the system allowed samples to be analyzed within 1.25 s, which is satisfactory for real-time soil sensing. The development of an automated soil extraction system was not particularly successful and requires considerable improvement. However, the concept of using ISFETs for real-time analysis of soil nitrates is sound. The extremely rapid response and low sample volumes required by the multi-sensor ISFET/FIA system make it a strong candidate for use in real-time soil nutrient sensing.

INTRODUCTION

Concern about the intensive application of nitrogen fertilizers, and their potentially adverse effects on the environment, has provided impetus for development of improved fertilizer management. Different soil nitrate levels, and different soil types with differing crop producing capabilities within a field, suggest that spatially varying the application of nitrogen fertilizers may be agronomically and environmentally beneficial. The cost and time required for the intensive sampling needed, using conventional sampling and analysis techniques, makes implementation of a variable-rate nitrogen fertilizer management system based on soil nitrate tests impractical. On-the-go real-time nitrate sensors are needed to locate areas of fields where additions of nitrogen fertilizer will be beneficial, and other areas where soil nitrate levels are such that additions of nitrogen fertilizer may have no economic benefit and could result in environmental degradation.

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Numerous studies have been conducted using commercial nitrate ion-selective electrodes in the development of soil nitrate tests (Dahnke 1971). Many commercial nitrate electrodes are based on a ion exchanger dissolved in an organic solvent to obtain an ion-exchanging liquid membrane that is insoluble in water. Davies, et al. (1972) used these commercial ion-exchanging liquids with polyvinyl chloride (PVC) to make polymer membranes. The majority of studies using ion-selective field effect transistors (ISFETs) has been conducted using polymeric membranes (Sibbald, et al., 1984; Sibbald, 1985; Tsukada, et al., 1987; Tsukada, et al., 1989; Tsukada, et al., 1989; Tsukada, et al., 1989). Birrell (1995) investigated the potential of other matrix membranes for use as ISFET membranes. Two ligands and two plasticizers were selected for further study in the development of nitrate ISFETs to be used in a FIA system for real-time soil analysis.

EQUIPMENT

A prototype automated soil extraction system was developed which isolated the addition of a soil sample from the introduction of the extracting liquid to prevent the solution from interfering with the metering of the soil. The system utilized a slide mechanism to move a constant volume of soil from the soil inlet to a position above one of eight chambers in a cylinder, which rotated to move the soil sample from station to station. A modified cross section, and perspective drawings of the automated soil extraction prototype, are shown in Birrell (1995). A sliding plate was used to translocate a volume of soil from the soil inlet to a position over one of the chambers of the rotating cylinder. The soil plunger pushed the soil from the soil slide into the chamber in the cylinder, which then rotated to move the soil sample to the next station. At Station 2, the extracting solution was sprayed into the chamber. After two more 45° increments, the initial chamber charged with soil was positioned at Station 4 above a Whatman[2] No. 42 filter. Filtration relied on the suction of a peristaltic pump that was used to pump the extract from the extract collection channel to the Flow Injection Analysis (FIA) system. At Station 8, the soil sample was above the waste channel, and an air nozzle above the soil chamber was used to clean the soil and liquid from the chamber.

The extract collection channel had two separate outlets, one positioned slightly higher than the other, and they were connected to separate channels on a peristaltic pump. The higher outlet was used to draw off any air in the collection channel and to collect a sample of the extract for analysis in the Lachat flow injection system (Lachat Quik Chem AE, Lachat Instruments, Milwaukee, WI), to compare the concentration of the automatically extracted samples with the concentration of a manually extracted sample. The lower channel was connected to the injection valve of the FIA system.

A servo-motor, which rotated the cylinder, was controlled using a 3-axis, servo-motor controller card (Omnitech, Model MC-3000), installed in a 486 personal computer. The position of the cylinder was monitored using a rotary encoder on the motor. The servo-motor controller

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[2] Trade names are used in this paper solely for the purpose of providing specific information. Mention of a trade name, proprietary product, or specific equipment does not constitute a guarantee or warranty by the U.S. Department of Agriculture or the University of Illinois, and does not imply the approval of the named product to the exclusion of other products that may be suitable.

also had digital output capabilities, which were used to control the operation of the air valves (that controlled the soil slide and soil plunger) and of the FIA injection valve. A QuickBASIC program was written to control the servo-motor controller. The program allowed the number of steps/s, and the angular rotation/step, to be independently changed. The washout time and injection cycle could also be changed.

The main section of the FIA system consisted of the multi-ISFET chip and holder, which was attached to an acrylic spacer using epoxy resin to direct the flow of liquid over the ISFET ion-selective membranes, and to protect the rest of the ISFET chip. The flow cell above the ISFETs formed a small mixing cell with a volume of approximately 0.008 μL. The top half of the cell was a stainless steel block of 40 mm by 25 mm by 12.5 mm, which was machined to match the acrylic spacer with minimal dead volume. The diameter of the bores in the block were 0.7 mm. Theoretically, a true reference electrode would be necessary, but in these tests a quasi-reference electrode was used instead.

The stainless steel flow cell was maintained at some potential (quasi-reference) with respect to ground for two reasons. First, the total potential on the ISFET gate had to be maintained at a certain threshold level, so the ISFET buffer amplifiers were not in a saturated state. Second, any static charges caused by stray voltages and the operation of the peristaltic pump were reduced.

The ISFETs were obtained from Hitachi Ltd., Tokyo, Japan, with the four-ISFET chip bonded to the ceramic carrier and the polyamide layer already applied, i.e., with the four sensor wells ready for membrane application. A thin layer of epoxy resin was carefully applied over the thin bonding wire and the bonding pads to protect the bonding wires. After the epoxy had cured, the ISFETS were ready for application of the ion-selective membranes. Two different ligands - tetradodecylammonium nitrate (TDDA) and methyltridodecylammonium chloride (MTDA), and two plasticizers - tri-(2-ethylhexyl)trimellitate (TOTM) and nitrophenyl octyl ether (NPOE), were used to obtain four different membrane cocktails which were placed on the different sensor surfaces. Additional detail on the preparation of the membranes, their placement on the chip surface, and the determination of the sensor gain and sensitivity are included in Birrell (1995). The four ISFETs were ISFET 1 (MTDA/NPOE), ISFET 2 (MTDA/TOTM), ISFET 3 (TDDA/NPOE), and ISFET 4 (TDDA/TOTM).

A Metrabyte DAS-HRES 16-bit A/D board connected to a 386 computer was used to collect the data using SNAPSHOT STORAGE SCOPE (HEM Data Corp.) data collection software. The power for the multi-ISFET chip was supplied by the A/D board and 4 analog channels were used in differential mode to collect the output voltages from the four ISFETs with respect to ground. A fifth channel was used to measure the voltage of the quasi-reference (flow cell) with respect to ground. A sixth channel was used to record the valve position to differentiate between the injection and washout portions of the cycle. The voltages were displayed on the screen of the computer and streamed to disk by the software for later analysis. Although the Metrabyte board was a 16-bit A/D board, there was crosstalk between the board clock and the analog channels which caused the resolution to be degraded to 13 or 14 bits.

METHODS AND PROCEDURE

The testing of the multi-ISFET, FIA system for soil analysis was carried out in two stages, the first using manually extracted samples and the second in which the soil to be analyzed was placed in the automated soil extraction system, and the extract fed directly into the FIA system.

This procedure was used to determine whether the major source of error was a result of the automated extraction or as a result of error in the nitrate analysis system. Based on previously conducted tests (Birrell 1995), an injection time of 0.5 s, washout times of 0.75 s and 2.5 s, and a nominal flowrate of 0.17 mL/s were used for these tests.

Analysis of Manual Soil Extractions

Soil extracts from ten different types of soils which represent a broad range of Illinois soils were tested in the multi-ISFET/FIA system. Loamy sand and sandy loam soils were not included in the manual and automated extraction tests, since the large sand particles jammed the soil metering mechanism, making the automated extraction procedure inoperable. Leached samples, prepared by leaching with distilled water, air-drying, and storing for 18 months, doubled the dataset. All soils were screened using a 2 mm sieve before testing. A manual extract of each soil was obtained by measuring out 20 ml of soil into an Erlenmeyer flask, adding 200 ml of 0.01 M $CuSO_4$ extracting solution, and shaking by hand for 2 min. The mixture was filtered through Whatman No. 42 filter paper to obtain the clear soil extract. Duplicated sub-samples of the soil extracts were analyzed using a Lachat Flow Injection system, using the cadmium reduction method, and these results were considered to be the actual nitrate concentration of the soil extracts. The mass of the soil used in the extraction was recorded and the extract concentration could be converted to soil nitrate in parts per million or any other common soil fertility units. However, since the work revolved around the development of the sensing system, the predicted concentrations in the soil extracts were compared directly.

The multi-ISFET/FIA system was calibrated before the analysis of manually extracted samples using two sets of standard solutions. The first set, which spanned a larger concentration range was prepared using successive dilutions, and consisted of 0.01, 0.001 and 0.0001 M $NaNO_3$ in a 0.01 M $CuSO_4$ solution. The second set, which spanned a limited concentration range, were prepared by pipetting a certain volume of a standard nitrate solution (0.02 M $NaNO_3$ in a 0.01 M $CuSO_4$) and standard chloride solution (0.02 M NaCl in a 0.01 M $CuSO_4$) into a volumetric flask and then diluted using 0.01 M $CuSO_4$. The second set consisted of 15 solutions, 5 consisting only of nitrates (0.00020, 0.00014, 0.00010, 0.00007 and 0.00005 M), 5 which included 0.0001 M NaCl in addition to the nitrates and 5 with 0.0002 M NaCl added. A complete discussion of the calibration test precedures and results is included in Birrell (1995).

Immediately after the system had been calibrated using the standard solutions, sub-samples of the twenty soil extracts were analyzed in a random order, using the multi-ISFET FIA with a 0.75 s washout time. Sub-samples of the twenty extracts were then rerun using a 2.5 s washout time. Once all 20 soil extracts had been analyzed using the 0.75 and 2.5 s washout times, the process was repeated for Replications 2 and 3, with the sample order rerandomized within each washout time.

The output of each ISFET was sampled at 1 kHz. The raw data were smoothed and the peak heights determined, and all response peaks in the data stream were retained. The mean and standard deviation for each test was then calculated, ignoring the highest and lowest peak height for each test. The outliers for each test were discarded if the absolute difference between individual peak heights (highest and lowest included) and the mean peak height, was greater than four times the standard deviation and greater than 5 percent of the mean height.

After the determination of the peak heights for each test, the Nernst slope (mV/decade change in ion concentration) and standard potential determined by the calibration analysis were used to estimate the nitrate concentration for individual peaks. The SAS Linear Regression (REG) procedure was used to determine the regression between the ISFET predicted concentration and the actual concentrations for each sensor, within each replication. The SAS General Linear Methods (GLM) procedure was used to test for significant differences in the analysis system among replications. During analysis, any soil extract with an actual nitrate concentration greater than 0.0005 M was excluded, since this level was outside the range of the calibration solutions and because approximately 0.0002 M (30 ppm soil N-NO_3) is an upper limit, beyond which additional nitrogen fertilizer is usually not recommended.

Analysis of Automated Soil Extractions

Manual extractions of the soils were obtained as previously described. Sub-samples of the manually extracted solutions were analyzed using the Lachat FIA system to determine the actual concentration in the soil extract. Calibration of the soil slide and soil plunger delivery system determined that it metered an average of 0.04 g of soil per cycle, equivalent to 0.12 g/s. The measurements (10 replications) showed a reasonable amount of variability within each soil and between different soils. Generally, the mass for each test was within 20 percent of the mean for that particular soil. Assuming a bulk density of 1.4 g/cc, the amount of extraction solution required (1:10 ratio) would be 1.8 mL/s. The actual flow rate from the peristaltic pump was 1.67 mL/s. Therefore, the theoretical soil:extractant ratio was slightly less than 1:10. The multi-ISFET/FIA system was calibrated prior to conducting the automatically extracted soil solution tests using the same procedure as for the manual tests; however, only a single replication of calibration tests were conducted before testing the soil extracts.

Immediately after calibration using the standard solutions, soil samples were analyzed using the multi-ISFET/FIA system. First, the automated soil extraction system was disconnected from the FIA system. Then a sub-sample of the manually extracted soil solution for the first soil in the randomized set was analyzed directly using the multi-ISFET/FIA system, with a 2.50 s washout time, followed by a test using a 0.75 s washout time. The automated extraction system was cleaned, reassembled and connected to the FIA system. Then the test of the first automatically extracted soil solution was conducted using a 0.75 s washout time, followed by a test using a 2.50 s washout time. The automated extraction system was then disconnected. A second sub-sample of the manually extracted soil solution was analyzed with a 0.75 s washout time, followed by a test using a 2.50 s washout time. Although the automated soil extraction system was disconnected from the FIA system during the tests of the manually extracted soil solutions, the soil extraction system was operated without any soil or fluid flow to ensure that any electro-magnetic interference produced by the automated extraction system would be present during all tests. This testing sequence was continued for all soils. If the automated soil extraction system malfunctioned during a test, it was disassembled, cleaned, reassembled and the test was repeated.

The response peak heights for the data collected from the automatically extracted soil solutions were highly variable and the outlier detection procedure used in the manual soil extraction tests was unsatisfactory. Outliers occurred at the beginning of the data stream for a soil, when the first peaks were a result of the injected sample consisting of a mixture of soil extract and the pure extractant solution. If the automated extraction proceeded successfully, the peaks increased in magnitude as the soil extract replaced more and more of the base solution in the samples being injected. At the end of the data stream for each sample, when the automated soil extraction system began to clog or run out of soil, the response peaks became very erratic. These data were visually inspected, and response peaks at the beginning of the test that resulted from mixed samples and those at the end of the test during the erratic period were discarded. The period for which the system operated correctly varied from test to test, so some tests resulted in a large number of response peaks being retained, while other tests resulted in very few response peaks. In three cases, no response peaks were retained. While this method relied on subjective judgment as to when the system was operating correctly, effort was made to minimize any subjective bias in the acceptance or rejection of response peaks.

The response peak heights for the standard solution and manually extracted soil solution test data that were collected in conjunction with the automatically extracted soil solution test data tended to be precise, and except for discarding peaks at the beginning and end of the test (to remove digital filter effects) all of the response peaks were used for further analysis.

Nernst slope and standard potential determined by the calibration analysis were used to estimate the nitrate concentration for individual response peaks. The SAS Linear Regression (REG) procedure was used to determine the regression between the ISFET predicted concentrations of the manually extracted soil solutions and the automatically extracted soil solutions, against the actual concentrations of the manually extracted soil solutions for each ISFET. The regression analysis was conducted using two different ranges of soil nitrate concentrations. The first regression was restricted to those soils with a soil nitrate concentration of less than 0.001 M, which resulted in the regression equation being estimated using extracted soil solutions with a concentration range of 0.000071 to 0.000309 M. The second regression was restricted to soils with a soil nitrate concentration of less than 0.002 M, which resulted in one more soil extract (0.00133 M) being used in the regression.

RESULTS AND DISCUSSION

Analysis of Manual Soil Extractions

The mean response peak heights for ISFET 1 generally were 30 percent greater than the corresponding peak heights for ISFETs 2, 3, and 4. This was consistent with the ISFETs' relative response to the calibration solutions (Birrell 1995). The mean response peak heights for ISFET 2 and ISFET 3 were very similar for each test. The mean response peak heights for ISFET 4 were slightly smaller than those for ISFET 2 and 3. The predicted concentrations for individual peaks for the manually extracted soil solutions were calculated for each test, using the Nernst slope and standard potential estimated during the calibration procedure. The plots of predicted concentration against the actual concentration with 0.75 s washout time show that sensor response during the first replication differed from the response during the last two replications (Fig. 1). The predicted concentration for the first replication was greater than the predicted concentration of the corresponding soils in Replications 2 and 3. The SAS General Linear Methods (GLM) procedure was used to test the significance of the replication blocks for the estimation of nitrate concentration and showed that the replication block was highly significant at the 1 percent level for all four ISFETs and both washout times, irrespective of the calibration range used to estimate the Nernst slope and standard potential (Birrell 1995). Differences in sensor response among replications could be a result of conditioning of the ISFET membrane as the tests progressed, drift of the membrane response, or a change in the dynamics of the junction potential between the pseudo-reference and the sample solution. However, the more likely explanation is that the flowrate parameters of the FIA system were slightly different, or the operation of the injection valve changed slightly after Replication 1 was completed.

The successful prediction of manual soil extractions depended largely on the correct estimation of the sensitivity response of the ISFET using the calibration solutions. Provided the correct calibration was used the slope of the regression between the predicted and actual concentration was approximately 1. However, the estimation of the sensitivity response did not significantly affect the correlation coefficient, since the use of the incorrect Nernst slope effectively changes the predicted concentration by some multiplication factor which is not reflected in the correlation coefficient. The correlation coefficient between the predicted and actual concentration for ISFET 1 was greater than 0.97 for two of the replications and 0.90 for the other replication, irrespective of the calibration range used, with a 0.75 s washout time (Birrell 1995). The correlation coefficients for ISFET 2 and ISFET 3 were between 0.85-0.88 and 0.84-0.90, respectively, when the lower calibration range was used with a 0.75 s washout time. However, the correlation coefficients for ISFET 2 and ISFET 3 were between 0.89-0.94 and 0.91-0.94, respectively, when the higher calibration range was used. The slightly lower correlations when the lower calibration range was used were due to the outliers in response peak height having a relatively greater effect, because the sensor's logarithmic response results in the predicted concentration of these outliers being grossly overestimated when the ISFET's sensitivity is underestimated. The correlation coefficients for ISFET 4 were between 0.90-0.97 for both calibration ranges, with a 0.75 s washout time.

The trends in correlation coefficients when a 2.5 s washout time was used were essentially identical to the corresponding trends for each ISFET when a 0.75 s washout time was used. In general, provided the correct ISFET sensitivity is used, the correlation coefficients between actual and predicted concentrations were greater than 0.90 for all of the ISFETs.

Analysis of Automated Soil Extractions

The predicted nitrate concentrations for individual response peaks were calculated for each test using the Nernst slope and standard potential estimated in the calibration procedure (0.00007-0.0002 M calibration range) for the automated soil extractions (Birrell 1995). A plot of the manually extracted soil solution's predicted concentrations against the actual concentrations of the corresponding manually extracted soil solutions is shown in Fig. 2, for the 0.75 s washout time. The slope of the regression line between the predicted and actual concentration is slightly less than the ideal 1:1 line for ISFET 1, slightly greater than the ideal for ISFET 2, identical to the ideal for ISFET 3 and somewhat less than the ideal for ISFET 4. However, all of the predicted concentrations are closely grouped around their respective regression lines which means that the different in the slope of their respective regression lines from the ideal is due to incorrect estimation of the Nernst slope and standard potential. Generally, the predicted concentration for all of the ISFETs for any single soil followed the same pattern. If the predicted concentrations of a particular soil were clustered above the regression line for one of the ISFETs, the predicted concentration for the same soil was also above their respective regression lines for the rest of the ISFETs. There are three possible causes of this type of variation of the predicted concentrations about their respective regression lines. First, the FIA flow dynamics may have changed slightly between soil tests; however, this was considered unlikely. Second, different interference ions in the different soil extracts may have affected the concentration predictions, but this explanation can also be considered unlikely, due to the high selectivity of the membranes. The third, and more likely, explanation is that the unknown junction potential at the quasi-reference was fairly constant within soils, but was not constant among different soils. Overall, the predicted concentrations of the soils samples were very close to their actual concentrations.

When using the prototype automated soil extraction equipment, the predicted nitrate concentrations for individual response peaks were calculated for each test using the Nernst slope and standard potential estimated in the calibration procedure (0.00007-0.0002 M calibration range). A plot of the automatically extracted soil solution's predicted concentrations against the actual concentrations of the corresponding manually extracted soil solutions is shown in Fig. 3, for the 0.75 s washout time.

The slopes of the regression lines between the predicted concentrations of the automatically extracted soil solutions and the concentration of the manually extracted soil solutions were considerably less than 1, for all of the ISFETs. The regression slopes were 0.43, 0.50, 0.43 and 0.28 for ISFET 1, ISFET 2, ISFET 3 and ISFET 4, respectively. Although the regression slopes were far from ideal, the predicted concentrations were grouped around their respective regression lines. However, the predicted concentrations for the automated analysis showed much greater variability than did those for the manual extractions. Similar to the predicted concentrations using manual extracts, the predicted soil concentrations for the automated extracts for any particular soil generally followed the same pattern for all four ISFETs, when compared to the predicted concentrations for the other soils.

The prototype automatic extraction equipment was not reliable, and problems observed during testing contributed to the inaccuracy of the nitrate concentration prediction. The sample flow from the automated extraction collection chamber was intermittent, and at times, air pockets were being drawn into the FIA system along with the extraction sample. Although it was impossible to measure, the flowrate of the sample stream was often less than that used during the calibration procedure. This was probably a result of the filter becoming clogged, causing a substantial negative pressure on the inlet side of the peristaltic pump which reduced the flowrate through the system. The intensity of these problems seemed to be dependent on the type and texture of the soil being analyzed. Occasionally the soil appeared to bridge above the soil slider, thereby reducing the volume of soil being delivered for extraction.

While the automated soil nitrate system did not accurately predict soil nitrates, the results did show some promise. The gross underestimation of the nitrate levels was probably a result of incomplete extraction of nitrate from the soil, and the inconsistent flow of the sample stream. While incomplete extraction of the nitrates from the soils was certainly the cause of some of the error, this probably was only a minor factor. The two most likely reasons for the poor recovery using the automated extraction procedure were the variation in the volume of soil metered out each cycle, and the change in the sample flow to the injection valve. The majority of the error is probably a result of the changes in sample flow. A decrease in the sample flowrate would translate into a decrease in the volume of the sample injected. Therefore, the sample volume would not correspond to the volume used in the calibration, causing the under-prediction of the nitrate concentration in the soil sample. The use of a different injection valve based on a sample loop would eliminate the consequences of changes in sample flowrate, provided sufficient sample volume is collected between injection cycles to refill the sample loop. The dilution ratio used in the automatic extraction could have been different from the nominal 1:10 ratio due to errors in the measured soil volume. However, provided the dilution ratio is constant, a correction factor could be used to account for the incorrect dilution ratio.

CONCLUSIONS

The multi-ISFET chip integrated into a FIA system can measure soil nitrate concentration in soil extracts. While the predictive capabilities of the four ISFETs, each having a different membrane composition, were slightly different, all of the ISFETs can predict soil nitrate level, provided the correct calibration numbers are used.

When precise, repetitive injection times and constant flowrates were maintained, the response of the sensors to soil extracts was very precise. The multi-ISFET/FIA system successfully predicted nitrates in manually prepared soil extracts. Operation of the multi-ISFET/FIA system without a true reference electrode may be an advantage, since the main source of errors in using ion selective electrodes for soil analysis is the reference electrode.

The prototype automated extraction system did not consistently provide soil extracts that could be analyzed by the FIA/ISFET system to predict soil nitrate levels. The predicted concentrations were much lower than the actual soil nitrate levels, although the predicted levels did show the same relative trends between the soils. Although the automated extraction procedure was not very successful, the results were encouraging and warrant further development.

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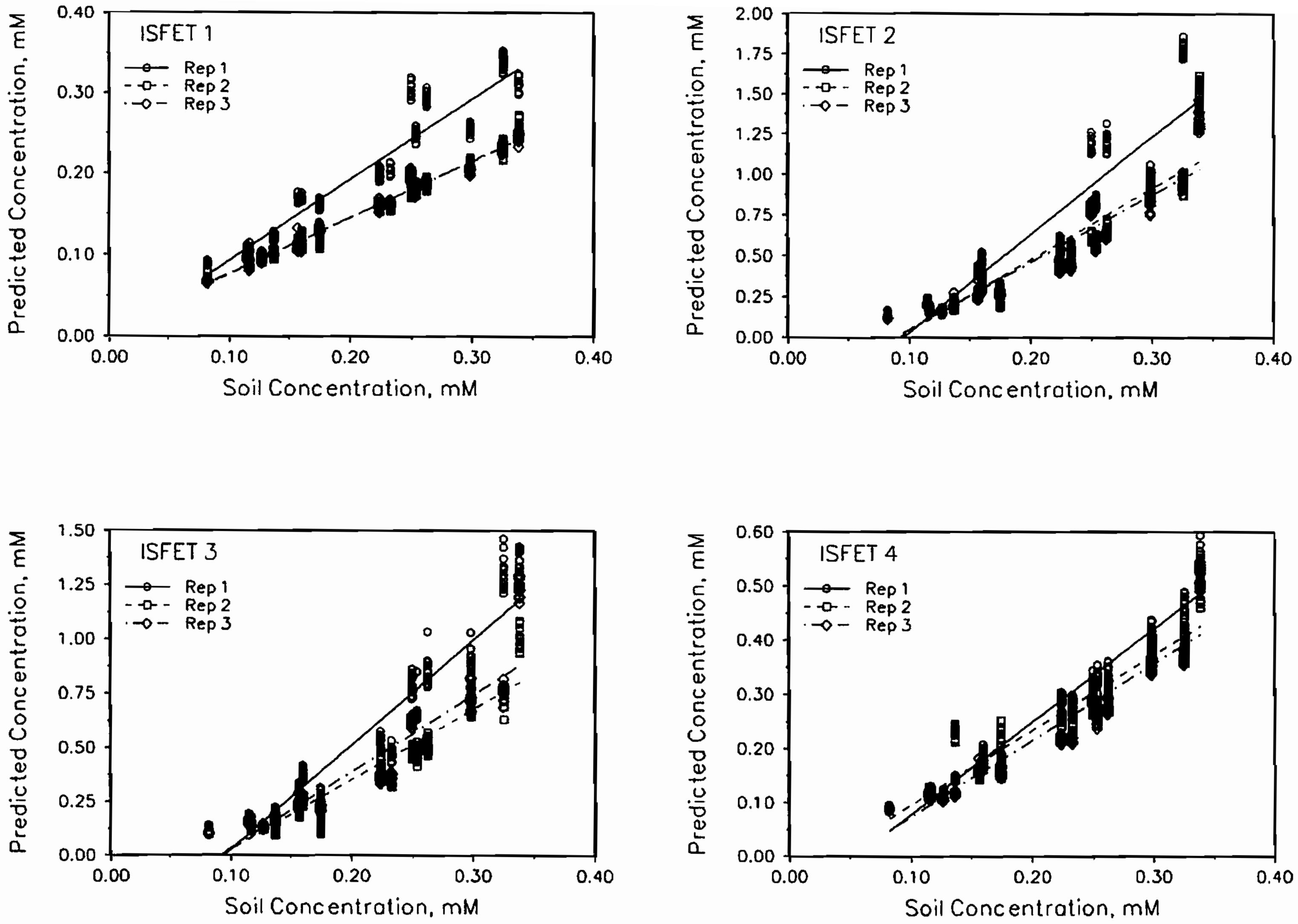

Figure 1. Predicted vs. actual soil extraction nitrate concentration for manually extracted soil solutions, calibrated using 0.00007 - 0.0002 M concentration range, with 0.75 s washout time.

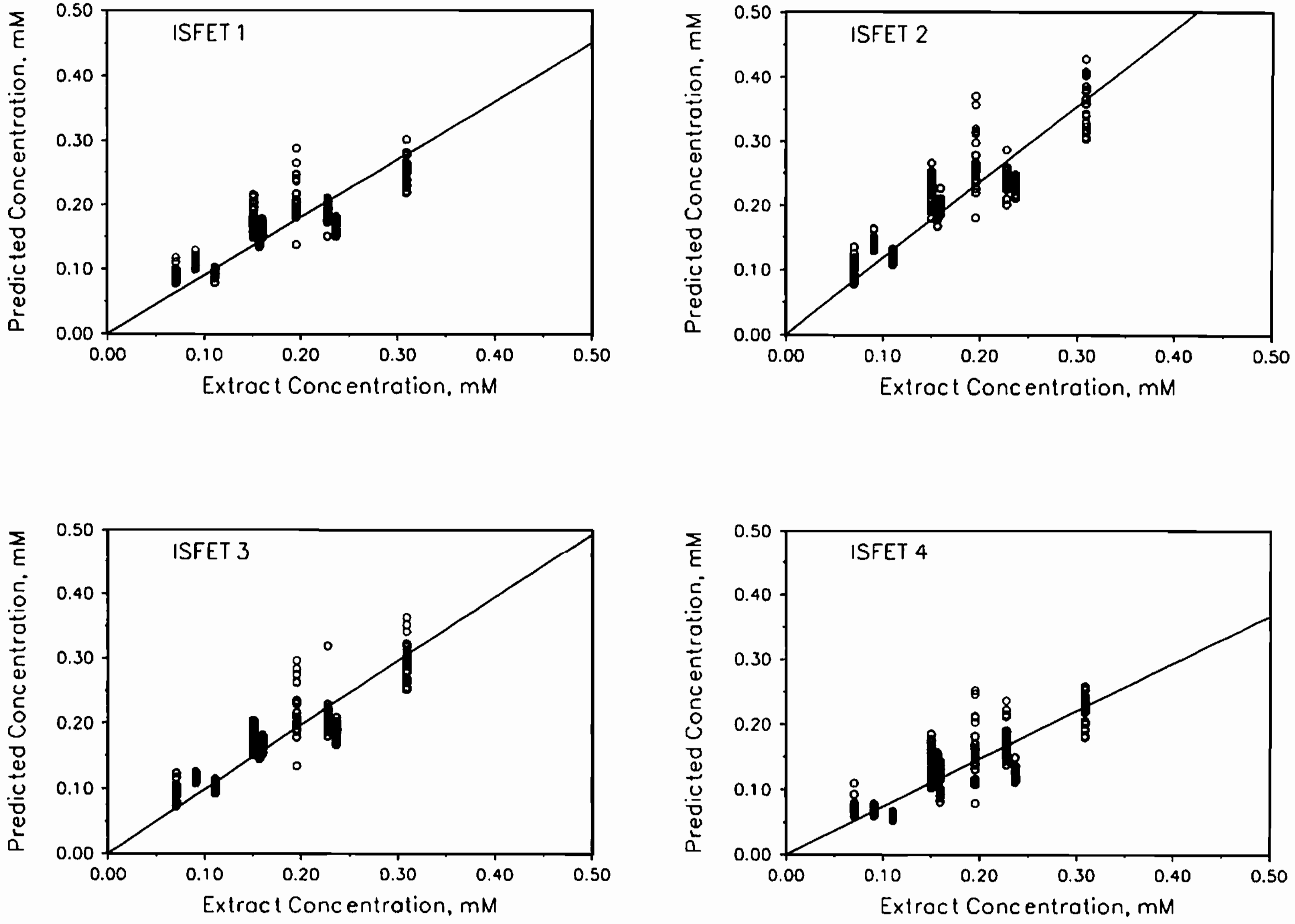

Figure 2. ISFET predicted concentration of manually extracted soil solutions vs. actual concentration (Lachat Analyzer) of same soil extracts, using 0.75 s washout time.

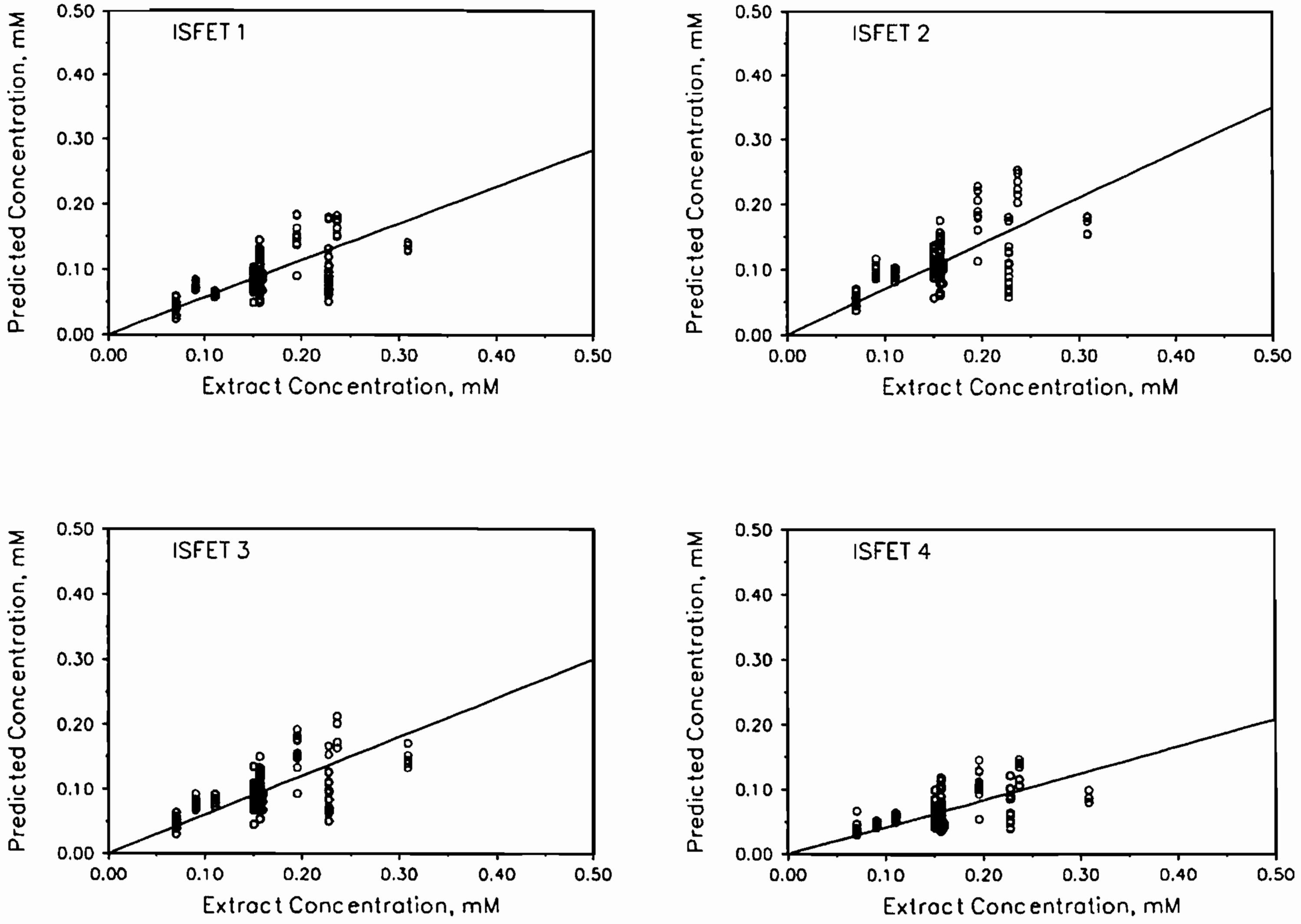

Figure 3. ISFET predicted concentration of automatically extracted soil solutions vs. actual concentration (Lachat Analyzer) of manually extracted soil solutions from the same soils, using 0.75 s washout time.

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