FLOW INJECTION SIMULTANEOUS DETERMINATION OF BASIC CATION PAIRS IN SOILS
ALEXANDRA M. R. FERREIRA,1 JOSÉ L. F. C. LIMA,2 AND ANTÔNIO O. S. S. RANGEL1

The growing demand for the determination of several analytes in a large number of soil samples explains the increasing interest in developing automatic methods of soil analysis. This paper reports the use of flow injection analysis (FIA) to perform automatically the simultaneous determination of the pairs K/Ca, Ca/Mg, Na/K, and Na/Mg in soils.

A dialysis unit was used to divide the sample plug into two different streams and also to create large dilution capacity. After appropriate treatment inside the manifold, the resulting plugs were directed to two detectors placed in parallel, thus allowing bicomponent analysis. Atomic absorption and flame emission spectrometry were used as detection processes.

The results obtained for an average of 25 soil samples by the developed FIA systems were in good agreement with those provided by the reference methods, i.e., the relative deviations were no larger than 3%. Sampling rates from 80 to 120 determinations per hour, and relative standard deviations below 3%, were obtained.

Routine soil analysis often requires the determination of its major content metal ions (sodium, potassium, calcium, and magnesium). The reference procedures described for these determinations (Soil and Plant Analysis Council 1992; Hesse 1972) are very time consuming: in addition to the process of analyte extraction from the soil sample, each resulting solution has to undergo the necessary treatment (dilution and eventual reagent addition) to adjust its composition to the requirements of the instrumental measurement (flame emission spectrometry for sodium and potassium and atomic absorption spectrophotometry for calcium and magnesium).

Because of the ever-growing demand for these determinations, it would be advantageous to develop continuous-flow systems to automatically carry out the determination of more than one species per injected soil extract sample. Different manifolds, based on flow injection analysis (FIA), have been described for multicomponent analysis in several matrices (Kubán 1993; Luque de Castro and Valcárcel 1986). These systems resort to one or more detection units and can be achieved by modifying the characteristics of the propulsion system (interactive change of the flow direction or stopped-flow), the injection system (multiple injection: series, parallel, or with coupled valves), the transport and reaction system (several reactors in parallel or closed circuit reactors), or even the detection unit (double beam or fast-response spectrophotometers). This last approach was used by Fang et al. (1985) for the simultaneous flame photometric determination of lithium, sodium, potassium, and calcium in soils and tap water. The use of inductively coupled plasma spectrometry (ICP) has also been described for simultaneous multielement determination in soil (Smith 1991), rock, and plant materials (Jacintho et al. 1981), either with sample discrete introduction or coupled to an FIA system. However, it involves very expensive equipment.

In this work, FIA manifolds incorporating the same detection systems described in the reference methods (flame emission and atomic absorption spectrometry) were devised to perform simultaneous determination of the ion pairs K/Ca, Ca/Mg, Na/K, and Na/Mg in ammonium acetate soil extracts. This simultaneous determination was made possible by using a dialysis unit to separate the injected plug into two different channels (donor and acceptor) and subsequently to direct each plug to different detectors placed in parallel.

MATERIAL AND METHODS
Reagents and solutions

Deionized water, with a specific conductance lower than 0.1 µS cm⁻¹, and analytical reagent grade chemicals were used for the preparation of the solutions.
The 1 M ammonium acetate extracting solution was prepared by mixing glacial acetic acid and concentrated ammonia, with the pH subsequently adjusted to 7 with either of these reagent solutions.

Sodium, potassium, and calcium 10,000 mg L\(^{-1}\) and magnesium 1000 mg L\(^{-1}\) stock solutions were prepared by rigorously weighing previously dried (at 100\(^\circ\)C) solid NaCl, KCl, CaCl\(_2\).2H\(_2\)O, and MgCl\(_2\).6H\(_2\)O, respectively, and dissolved in 1 M ammonium acetate. The standards used for establishing the calibration curves were prepared by dilution of the stock solutions in 1 M ammonium acetate. The calcium and magnesium standards used for the reference method presented a lanthanum (III) concentration of 10,000 mg L\(^{-1}\).

The lanthanum (III) stock solution was prepared from solid La\(_2\)O\(_3\), and presented a 100 g L\(^{-1}\) concentration in lanthanum and 0.6 M in HCl.

**Instrumentation and flow injection manifold**

The determinations of sodium and potassium were carried out in two Jenway PFP7 flame photometers using an air-butane flame. Calcium and magnesium determinations were performed with GBC 902 atomic absorption spectrophotometers with an air-acetylene flame. The detection systems were connected to a double-channel Kipp & Zonnen (Delft, Holland) BD 112 chart recorder.

In the FIA systems, solutions were propelled by Gilson (Villers-le-Bel, France) Minipuls 2 and Minipuls 3 peristaltic pumps and Gilson propulsion tubes. Standards and soil extracts were injected with a Rheodyne Type 50 injection valve.

The connections between the different components of the manifolds were made with 0.8 mm i.d. Omnifit Teflon tubes, Gilson end-fittings and connectors, and perspex home-made Y-shaped joints used as confluence or stream-splitting points.

The dialysis unit incorporated in the manifolds included a flow channel that was 2 mm wide, 0.5 mm deep, and 140 mm long (linear path). A Tecator 5588 0002 dialysis membrane separated the donor and the acceptor stream.

**Reference methods**

The reference methods used for comparison purposes were carried out as described in the Soil and Plant Analysis Council (1992) handbook. The soil samples were air-dried, ground, and sieved (in a 1-mm sieve). The extracts for analysis were prepared as follows: 5 g of soil were shaken for 5 min with 25 ml of 1 M ammonium acetate and then vacuum filtered through a Whatman 542 filter paper. The resulting clear extracts were used for carrying out the determinations. After establishing the calibration curves for Na and K determinations in the flame photometer and of Ca and Mg determinations in the atomic absorption spectrophotometer, the extracts were diluted by a trial and error approach in order to fit their composition to the linear range of each calibration plot. All the determinations were performed in triplicate for each extract.

**RESULTS AND DISCUSSION**

Flow injection systems were developed to carry out the simultaneous determination of the pairs K/Ca, Ca/Mg, Na/K, and Na/Mg, using atomic absorption and flame emission spectrometry as detection processes. In order to perform two analyte determinations with the same injected extract, a dialysis unit was incorporated in the manifold so that the sample plug could be divided between the donor stream and the acceptor stream and, subsequently, direct each portion to a detection system. After the dialysis process, the analyte concentration in the donor stream remains almost unaltered; consequently, this plug has to undergo extensive dilution before its introduction into the detection system. On the other hand, because of the low yield of the dialysis process, the plug in the acceptor stream may present a concentration within the working range of the detection system if the manifold parameters are adjusted conveniently.

The configuration of the two developed flow injection manifolds was essentially decided by the extent of dilution needed for each determination. For each determination, the parameters were optimized so that a linear working range could be obtained that would include the concentration interval usually found for each metal in the soil extracts (Soil and Plant Analysis Council 1992). In the following results presentation, the linear concentration range corresponding to each determination is presented: the lower limit corresponds to the methodology detection limit, calculated as three times the standard deviation of the system background noise; the upper limit was estimated from the calibration plots for each determination. All the results are expressed in milligrams of analyte per kilogram of soil.
Simultaneous determination of K/Ca and Ca/Mg

The concentration of these ions in the ammonium acetate soil extracts is much higher than the linear working concentration range of the detection systems used. For this reason, a manifold able to provide a large dilution needed to be devised. To achieve this goal, a manifold with a dialysis unit and a stream-splitting point was developed (Fig. 1).

The determination that required the largest dispersion was selected to be performed in the acceptor stream. Thus, a less complicated system could be created for adjusting the plug remaining in the donor stream to the detection system characteristics. For the K/Ca determination, calcium was measured (atomic absorption spectrometry) in the acceptor stream and potassium (flame emission spectrometry) in the donor stream. For the Ca/Mg pair determination, magnesium was determined in the acceptor stream (atomic absorption spectrometry) and calcium in the donor stream (atomic absorption spectrometry).

The sample was injected into a carrier stream and led to the dialysis unit through a 50-cm-long tube (L2). The ions in the dispersed sample plug diffuse to the acceptor channel across the dialysis membrane, driven by the concentration gradient. The analyte that diffused to the acceptor channel was then directed to a confluence (Y) for a 5000 mg L⁻¹ lanthanum (III) solution addition in order to minimize chemical interference in the atomization process (determination of calcium and magnesium).

Inasmuch as the dialysis process produced extensive dilution, manifold parameters and instrumental conditions were adjusted to obtain maximum sensitivity. Equal flow-rates were imposed on both sides of the membrane. Additionally, the flow-rate at the nebulizer entrance was adjusted with the confluent stream (Qo) in order to correspond approximately to the intrinsic uptake rate of the spectrometer and, thus, to the maximum sensitivity conditions. However, even for the optimized parameters, the dialysis produced a dilution extent that was larger than that required to perform the measurements in a linear range. Consequently, the detection limit was too high, not allowing determinations of extracts with lower metal concentrations. Therefore, a decision was made to increase the dialysis efficiency by acidifying both the donor and acceptor channels with 0.2 M HCl. This concentration was found to be the minimum necessary to increase dialysis efficiency.

The part of the analyte remaining in the donor stream had to be submitted to extensive dilution before its introduction in the other detector. To achieve this without significantly diminishing the sampling rate, a stream-splitting point (X) was used. The sample was divided, and one part was wasted while the other was directed to the spectrometer. This way, the amount of sample flowing to the detector was significantly reduced, as was the sample plug extent, thus maintaining a good sampling rate. The reduced portion of the analyte was then dispersed in a flow tube (L3) and underwent another dilution in confluence Z. This confluence allowed an increase in the dispersion level as well as the addition of a lanthanum (III) solution for the calcium determination.

Once this configuration was established, some parameters were adjusted to obtain the best conditions for the determination of each pair. An injection volume of 240 µl was used for both pairs, K/Ca and Ca/Mg, because it was the minimum value for obtaining good sensitivity and reproducibility.

For the calcium determination, correspondent to the analysis of the pair (Ca/Mg), a larger dispersion should be obtained. The Qo stream was
increased from 0.45 to 0.70 ml min⁻¹, thus decreasing the amount of analyte flowing to the detector. Because this stream splitting was still not sufficient for achieving the necessary dilution (about 200-fold), the sensitivity of the atomic absorption measurement was decreased by rotating the burner head about 30°.

With this manifold, it was possible to perform 80 determinations per hour for the pair K/Ca in the range of 0.5 to 500 mg kg⁻¹ for potassium and 100 to 2500 mg kg⁻¹ for calcium. The system allowed 100 determinations per hour of the pair of ions Ca/Mg in the range of 40 to 250 mg kg⁻¹ for calcium and 10 to 350 mg kg⁻¹ for magnesium.

It should be stressed that these metal concentrations usually present in soils (Soil and Plant Analysis Council 1992), are completely included in the above-mentioned intervals, and, therefore, the sample extracts can always be injected directly into the flow injection systems.

Simultaneous Determination of Na/K and Na/Mg

As the dilution level required for the determination of available sodium was lower than for potassium or magnesium determinations, we opted to use the sample plug remaining in the donor stream to carry out the sodium measurements. This way, it would not be necessary to promote a large dilution after the dialysis unit, and no increase in the manifold complexity would occur with inclusion of a stream splitting followed by a confluence. The potassium and magnesium determinations were performed in the acceptor stream, this being the dialysis process sufficient to adjust the soil extracts to the linear range of the spectrometers. The injection volume was maintained at 240 μl. The manifold developed for these determinations is presented in Fig. 2.

The analyte that diffused to the acceptor channel Q₃ was combined with a stream of water (determination of potassium) or a 5000 mg L⁻¹ lanthanum (III) solution (determination of magnesium) in confluence Y. This confluent channel (Q₃) provided a flow-rate at the entrance of the nebulizer similar to the natural spectrometer's uptake rate. The sample plug that remained in the donor stream was combined with a water stream in confluence X, with a flow rate (Q₁) selected to impose an overpressure at the nebulizer entrance as a way to reach the required dispersion level in the subsystem developed for the determination of Na. This overpressure produced a decrease in the nebulization efficiency of the atomization process, which was not compensated for an additional amount of analyte entering the nebulizer, thus contributing to a further decrease of the analytical signal. This strategy was sufficient to provide the dispersion necessary for performing the determinations in a linear dependence range.

For the determination of the pair Na/K, the dialysis efficiency was augmented by the use of 1 M HCl in the acceptor channel (Q₄), whereas for the determination of the pair Na/Mg, both sides of the membrane (Q₂ and Q₃) were acidified with 0.2 M HCl.

It was possible to perform 120 determinations per hour of the Na/K pair in the range of 0.95 to 300 mg kg⁻¹ sodium and 1.7 to 1000 mg kg⁻¹ for potassium. The same manifold allowed a sampling rate of 100 determinations per hour of Na and Mg, allowing determinations in the range of 0.02 to 250 mg kg⁻¹ for sodium and between 19 and 400 mg kg⁻¹ for magnesium. The concentrations of these elements normally found in soils are included in the above mentioned intervals, thus, soil extracts can be injected with no prior treatment.
Analysis of soil samples

The soil extracts, prepared as described in the Methods section, were injected into the flow injection manifolds, and the concentration was calculated by interpolation in the previously established calibration plots. Every standard and soil extract was injected in triplicate (Fig. 3).

In order to assess the accuracy of the FIA results, analyses of soil extracts using the flow injection manifolds and the reference methods (Soil and Plant Analysis Council 1992) were carried out. For comparison purposes, a relation of type \( C_r = C_0 + SC_r \) was established, with \( C_r \) representing the results obtained with the FIA methodology and \( C_r \) those provided by the reference methods (Table 1).

There is a good agreement between the two methodologies, as can be seen by the slope and intercept values. Additionally, the observed relative deviations between the two methodologies were, typically, less than 3%.

In order to evaluate the methodology reproducibility, the relative standard deviation was calculated from 10 consecutive injections of three soil samples, with concentrations covering the analytical range for each determination. The reproducibility was also good, with 3% the highest relative standard deviation observed.

A sampling-rate of 80 to 120 determinations per hour was achieved. This was better than the rate provided by the reference methods and ICP.

---

**TABLE 1**

Comparison of the results obtained in the soil extract determinations by the developed bicomponent FIA systems (\( C_r \)) and by the reference methodology (\( C_r \)), atomic absorption spectrophotometry (AAS) and flame emission spectrometry (FES). Dispersion levels and sampling rates obtained with the developed FIA systems

<table>
<thead>
<tr>
<th>Ion pairs</th>
<th>Parameters of equation ( C_r = C_0 + SC_r )</th>
<th>Characteristics of the FIA systems</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( C_0 ) (mg kg(^{-1})) S R(^2) Number of samples analyzed</td>
<td>RSD(^b)% Dispersion coefficient Overall sampling rate(mg L(^{-1}))</td>
</tr>
<tr>
<td>Na (FES)/K (FES)</td>
<td>Sodium 2.8 0.95 0.9998 25</td>
<td>&lt;1 13 120</td>
</tr>
<tr>
<td></td>
<td>Potassium 5.7 0.98 0.9990 25</td>
<td>&lt;1 86</td>
</tr>
<tr>
<td>K(FES)/Ca(AAS)</td>
<td>Potassium 1.4 0.995 0.998 25</td>
<td>&lt;1 48 80</td>
</tr>
<tr>
<td></td>
<td>Calcium 6.8 0.983 0.9990 25</td>
<td>&lt;3 235</td>
</tr>
<tr>
<td>Ca (AAS)/Mg (AAS)</td>
<td>Calcium 15.4 1.00 0.997 25</td>
<td>&lt;3 21 100</td>
</tr>
<tr>
<td></td>
<td>Magnesium 2.9 1.02 0.998 25</td>
<td>&lt;3 400</td>
</tr>
<tr>
<td>Na (FES)/Mg (AAS)</td>
<td>Sodium 0.9 1.02 0.9990 23</td>
<td>&lt;2 11 100</td>
</tr>
<tr>
<td></td>
<td>Magnesium 1.5 1.01 0.998 23</td>
<td>&lt;3 417</td>
</tr>
</tbody>
</table>

\(^a\) Correlation coefficient.

\(^b\) Relative standard deviation obtained from 10 consecutive injections of soil extracts.

---

Fig. 3. Recorder output obtained for simultaneous determination of the pair sodium/potassium in soil extracts using two flame emission spectrometers as detection systems. Injected standard solutions: \( A = 10; B = 20; C = 30; D = 40; E = 60; F = 80 \) mg L\(^{-1}\) of sodium; and \( A' = 20; B' = 40; C' = 80; D' = 100; E' = 120; F' = 160 \) mg L\(^{-1}\) of potassium.

In fact, one can estimate that only from 20 to 40 determinations per hour can be performed using the last two methodologies.
CONCLUSIONS

The developed multicomponent FIA systems are superior alternatives to the conventional manual reference procedures because they permit automatic soil extract preparation and the simultaneous instrumental measurement of pairs of ions, with high sampling rates. The implementation of the developed manifolds in common soil analysis laboratories is accessible as they make use of the same detection systems employed for the reference methods and additional low cost FIA apparatus.

It should be stressed that using only two manifolds, it was, nevertheless, possible to determine the four ions in four different combinations, which allowed savings on reagents and soil extract. In fact, lanthanum (III) consumption is reduced approximately tenfold compared with the reference methodology.

The dialysis process was shown to be a good way both for obtaining an FIA system with a large dilution capacity and for dividing the plug into two channels, thus allowing multidetermination by using two detectors in parallel.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the financial support from JNICT, through project PEAM/C/TAI/259/93. One of the authors (A. M. R. Ferreira) thanks JNICT for Grant BD/2110/92-IE.

REFERENCES


