Development and application of potentiometric methods of characterizing potassium in soils and micaceous minerals

Richard Edmond Farrell
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DEVELOPMENT AND APPLICATION OF POTENTIOMETRIC METHODS OF CHARACTERIZING POTASSIUM IN SOILS AND MICACEOUS MINERALS

Iowa State University

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Development and application of potentiometric methods of characterizing potassium in soils and micaceous minerals

by

Richard Edmond Farrell

A Dissertation Submitted to the Graduate Faculty in Partial Fulfillment of the Requirements for the Degree of

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# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>GENERAL INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>Objectives</td>
<td>4</td>
</tr>
<tr>
<td>Current Information and Related Work</td>
<td>4</td>
</tr>
<tr>
<td>Explanation of Dissertation Format</td>
<td>8</td>
</tr>
<tr>
<td>SECTION I. CELL AND PROCEDURE REQUIREMENTS FOR ION-SELECTIVE ELECTRODE</td>
<td>10</td>
</tr>
<tr>
<td>DETERMINATIONS OF POTASSIUM</td>
<td></td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>11</td>
</tr>
<tr>
<td>INTRODUCTION</td>
<td>13</td>
</tr>
<tr>
<td>EXPERIMENTAL</td>
<td>16</td>
</tr>
<tr>
<td>Reagents</td>
<td>16</td>
</tr>
<tr>
<td>Electrodes</td>
<td>16</td>
</tr>
<tr>
<td>Apparatus and Experimental Techniques</td>
<td>16</td>
</tr>
<tr>
<td>Evaluation of Electrode Behavior</td>
<td>17</td>
</tr>
<tr>
<td>RESULTS AND DISCUSSION</td>
<td>18</td>
</tr>
<tr>
<td>Reference Electrodes</td>
<td>18</td>
</tr>
<tr>
<td>Comparison of K-ISEs</td>
<td>32</td>
</tr>
<tr>
<td>Ammonium Ion Interference</td>
<td>35</td>
</tr>
<tr>
<td>LITERATURE CITED</td>
<td>44b</td>
</tr>
</tbody>
</table>

| SECTION II. AN EVALUATION OF ION-SELECTIVE ELECTRODE METHODS OF         | 46   |
| DETERMINING EXCHANGEABLE POTASSIUM IN SOILS                              |      |
| ABSTRACT                                                                | 47   |
| INTRODUCTION                                                            | 49   |
| EXPERIMENTAL                                                            | 52   |
| Potassium Extractions                                                   | 52   |
| Analytical Determinations of Potassium                                  | 52   |
### TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>RESULTS AND DISCUSSION</td>
<td>57</td>
</tr>
<tr>
<td>Barium Chloride Exchangeable Potassium</td>
<td>57</td>
</tr>
<tr>
<td>Ammonium Acetate Exchangeable Potassium</td>
<td>63</td>
</tr>
<tr>
<td>LITERATURE CITED</td>
<td>70</td>
</tr>
<tr>
<td>SECTION III. CONSTRUCTION AND EVALUATION OF A POTASSIUM-SELECTIVE TUBE-MOUNTED MEMBRANE ELECTRODE</td>
<td>73</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>74</td>
</tr>
<tr>
<td>INTRODUCTION</td>
<td>75</td>
</tr>
<tr>
<td>EXPERIMENTAL</td>
<td>76</td>
</tr>
<tr>
<td>Electrodes</td>
<td>76</td>
</tr>
<tr>
<td>Apparatus and Experimental Techniques</td>
<td>77</td>
</tr>
<tr>
<td>RESULTS AND DISCUSSION</td>
<td>79</td>
</tr>
<tr>
<td>LITERATURE CITED</td>
<td>87</td>
</tr>
<tr>
<td>GENERAL CONCLUSIONS AND DISCUSSION</td>
<td>88</td>
</tr>
<tr>
<td>ADDITIONAL LITERATURE CITED</td>
<td>91</td>
</tr>
<tr>
<td>ACKNOWLEDGMENTS</td>
<td>96</td>
</tr>
</tbody>
</table>
GENERAL INTRODUCTION

Potassium (K) is the seventh most abundant element in the earth's crust [11]. The amounts of potassium, however, vary from an average of 2.3-2.6\% (w/w) in the total lithosphere [11,50], to only 0.83-1.4\% in soils [30,50]. Obviously, pedogenesis involves a considerable loss of potassium. On the other hand, the fact that potassium is still the seventh most abundant element in soils [30] indicates that its mineralogy and chemistry offers considerable resistance to this loss. The exact nature and balance of the forces controlling the level of potassium in the soil are still unclear. Thus, the role and fate of potassium in soil development continue to attract a great deal of attention.

Most of the potassium in soils occurs in the K-feldspars, micas, and micaceous clay minerals [49,50]. Thus, the crystal structure, properties, and weathering of these minerals have been studied extensively and related to the behavior of potassium in soils [2,6,50]. From various reviews of mineral weathering [6,49,50], it is evident that many factors and processes have to be considered. With micas, the exchange of interlayer potassium has probably received the most attention but the dissolution of either mineral has to be accounted for as well. Moreover, an overall characterization of potassium in soils must include the water-soluble, exchangeable and slowly-releaseable forms of potassium [50,53,58]. The interrelationships between these forms of potassium and the structural potassium in minerals play a major role in the chemical properties and development of soils [21]. At the same time, it is these forms of potassium that must be supplied in large enough amounts at adequate rates.
to support the growth of plants. Because potassium is the only univalent
cation that is essential for all living organisms [13,59] and it must
ultimately come from the soil or K-mineral deposits [6,49], an overall
integration of soil-plant relationships with the chemistry and mineralogy
of soil potassium is necessary. A fundamental requirement for all this
research is the availability of appropriate methods of determining the
levels and dynamics of potassium under a variety of conditions.

Prior to 1950, wet chemical methods of measuring potassium with
gravimetric, colorimetric, and titrimetric procedures were predominant
[26]. These methods provide a high degree of accuracy and precision and
are still used as reference methods for the standardization of new tech­
niques, but they are time-consuming and not well-suited for many of the
potassium analyses needed today. With the introduction of the flame
photometer in the early 1950s, atomic emission spectrometry (AES) became
the common analytical method for potassium analysis [56,59]. Indeed, the
AES and subsequently developed atomic absorption spectrometry (AAS)
methods have remained the dominant ones in nearly all agricultural and
clinical laboratories for nearly 30 years. Recently, ion chromatography
(IC) has been used to determine ion combinations that include potassium
and has been applied successfully to environmental and agricultural
samples [5,19]. All these methods have common limitations, however, in
that they are not suited for measurements of potassium variability within
samples; they involve "destructive" analyses, i.e., the original sample
cannot be retained for further study, and they are not adaptable to in
situ analyses or the monitoring of potassium exchanges.
As our knowledge of the chemistry of potassium in minerals and soils has continued to grow so has our need to develop new analytical techniques for measuring the various structural and extractable fractions of the potassium. Methods of electron probe microanalysis (EPMA) and instrumental neutron activation analysis (INAA) have been used to determine potassium as it exists in solid samples of mica and soil, respectively [46,51]. Potentiometric methods of analysis [3,54] that employ potassium ion-selective electrodes (K-ISEs), on the other hand, offer the unique means of measuring the soluble, exchangeable and slowly-releasable forms of potassium without separating the solution phase from the soils or minerals. The advantages in using K-ISEs include (1) simple, nondestructive analysis, (2) potassium ion activity rather than concentration measurements, (3) automated analysis, (4) continuous monitoring capabilities, and (5) the possibility of in situ potassium determinations. The main limitation of the K-ISEs is their imperfect selectivity for potassium ions. Because the electrodes may respond adversely to some of the conditions imposed by the techniques that are used to extract the various fractions of potassium [14], accurate potentiometric measurements of potassium in soil and mineral systems have been difficult to achieve.

Recently, the highly-selective valinomycin-based K-ISEs and a new generation of automated potassium analyzers employing these ISEs have become commonplace in clinical laboratories [11,59]. At the same time, however, the enormous potential of using these K-ISEs in soil and mineral analyses has remained virtually unexplored [54]. Even though potassium remains one of the more difficult ions to handle by potentiometric
methods, it is evident that ISE technology has advanced enough to warrant its adaptation to the conditions encountered with soils and minerals. Ultimately, it is expected that K-ISEs will provide an excellent means of carrying out routine analyses for potassium and will lead to new ways of characterizing the forms, reactions and relevance of potassium in soils and minerals.

Objectives

The objectives of this study were to establish the basic cell requirements and procedures for the potentiometric determination of potassium in soil extracts; to evaluate ion-selective electrode methods for determining the exchangeable potassium in soils; and to design new K-ISEs with a variety of plasticizers, matrices, and K-selective ionophores to permit the determination of potassium in partially nonaqueous solutions (i.e., 60% acetone solutions that are used to dissolve potassium tetraphenylboron).

Current Information and Related Work

An ion-selective electrode is defined as an electrochemical sensor, the potential of which is linearly dependent on the logarithm of the activity of a given ion in solution [7]. However, few, if any, ISEs are exclusively selective for a single ionic species. The response of an ISE to its primary ion in the presence of interfering ions can be described by the extended Nicolsky equation [42]:

\[ E = E_1^O + \frac{RT}{z_i F} \ln a_i + \sum_j k_{ij} \text{Pot} (a_j)^{z_i/z_j} \]  

(1)
where $E$ is the electrode potential and $E^o_i$ is the standard potential of the electrode; $R$, $T$, and $F$ are the gas constant, absolute temperature, and Faraday constant, respectively; $z_i$, $a_i$ and $z_j$, $a_j$ are the valence and activity of the primary ion $i$ and interfering ions $j$, respectively; and $k_{ij}^{\text{Pot}}$ is the potentiometric selectivity coefficient, which defines the ability of an ISE to distinguish between ions in the same solution [7].

For an electrode exhibiting ideally specific behavior, or a situation where $a_i >> k_{ij}^{\text{Pot}} (a_j)^{z_i/z_j}$, the Nicolsky equation is reduced to the classical Nernst equation:

$$E = E^o_i + \frac{RT}{z_i F} \ln a_i$$

(2)

which for a system with a monovalent cation in a solution at 22°C predicts a 58.56 mV potential response for each 10-fold change in $a_i$.

In addition to being identified in terms of their response to the primary ion (e.g., K-ISE), each ISE may be classified according to the nature of the ion-selective material. Five categories are generally recognized: (1) solid-state membrane electrodes, based on single crystal, pressed polycrystalline pellets, and heterogeneous precipitates; (2) glass membrane electrodes, formed from aluminosilicate glasses; (3) liquid ion-exchanger membrane electrodes, consisting of an organic, water-immiscible liquid phase incorporating mobile ionic or ionogenic compounds; (4) neutral carrier liquid membrane electrodes, consisting of an organic solution of a neutral, ion-specific complexing agent held in an inert polymer matrix; and (5) miscellaneous electrodes, including gas-sensing and enzyme electrodes, and ion-sensitive field effect transistors.
(ISFETs). Various ISEs in each category have been shown to be K-selective, and to respond to potassium ion activities ($a_{K^+}$) in a near-Nernstian fashion.

Following the development of the pH sensitive glass electrode in 1906 [9] and the subsequent elucidation of the "alkaline error" at high pH by Lengyel and Blum in 1934 [29], the literature dealing with the development and application of ISEs has increased rapidly [8,28,38]. The earliest K-ISEs were the zeolite, clay, and collodion membranes of Marshall and co-workers [32-35] and Sollner [52]. However, because they were very fragile and lacked selectivity for any one ion, these electrodes were abandoned in favor of the more rugged and K-selective glass membrane electrodes described by Eisenman [12]. Work with these electrodes showed their cation selectivity to be a function of the glass composition, and the NAS 27-04 (i.e., 27 mol % $Na_2O$, 4 mol % $Al_2O_3$, 69 mol % $SiO_2$) glass composition to have the greatest selectivity for potassium. During this period (i.e., 1955-1965), the development of a variety of K-ISEs based on the incorporation of different organic [55] and inorganic [16,20] ion-exchangers and ion-exchange resins [60] into paraffin, plastic, and silicone rubber matrices met with only marginal success. In 1964, Moore and Pressman [37] reported that certain neutral macrocyclic antibiotics induced mitochondrial cation permeation; and thereby, focused attention on the highly K-selective macrocycle valinomycin. Five years later, the first K-selective liquid membrane electrode, using a filter disc saturated with valinomycin in diphenyl ether, was described [44]. This electrode yielded selectivity ratios of 4000:1 for $K^+$ over $Na^+$ and 100:1 for...
K\(^+\) over NH\(_4\)^+ as compared to ratios of 10:1 and 1:1, respectively, for the glass electrode [3]. A similar electrode described by Frant and Ross [17] exhibited even higher selectivity for K\(^+\) with respect to Na\(^+\), but a somewhat lower selectivity over NH\(_4\)^+. These liquid membrane electrodes were inconvenient to handle and service, and had relatively short lifetimes of only a few weeks. It was not long, however, before valinomycin was successfully incorporated into PVC [15] and silicone rubber [43] matrices for easier handling and longer lifetimes (i.e., several months to more than a year). Other macrocyclic compounds such as the "crown ethers" discovered by Pederson [42] have been used in the preparation of K-ISEs [36,47], but they have yielded little or no advantage over the valinomycin-based electrodes. More recently, a variety of crown ether derivatives, e.g., the bis-crown ethers [24,25], have been synthesized and shown to yield K-ISEs with somewhat higher selectivities for K\(^+\) over NH\(_4\)^+. In addition, reductions of the size of K-ISEs based on valinomycin and the crown ethers have been achieved with K-sensitive coated-wire electrodes (K-CWEs [18]) and K-sensitive field effect transistors (K-ISFETs [23]).

In 1961, Mortland [39] used a cationic glass electrode (CGE) to determine the concentration of Mg-exchangeable potassium in soil suspensions. A comparison of these CGE values with those obtained by analyzing the supernatant solution by AES showed the results for the two methods to be highly correlated (r=0.90); although the CGE values were significantly higher. The differences in the potassium values were attributed to interferences from exchangeable sodium and ammonium ions in the suspensions. Despite this lack of selectivity for potassium, which is
now well-documented [3,28], these electrodes have been used in soil and mineral studies with varying degrees of success [14,27,31,40]. And, although some reports have shown that NH$_4^+$ interferences can be reduced by maintaining a very high solution pH [22] or by complexation with formaldehyde in mildly alkaline solutions [14], the difficulties with varying levels of Na$^+$ in the soil solutions have not been resolved with the CGEs.

Even though the valinomycin-based K-selective electrodes (VKEs) have been available for more than a decade, and their tolerance to Na$^+$ is well-known [3,17], there have been relatively few reports of their being used with soil or mineral systems. However, determinations of potassium activity-concentration relationships in soil:water extracts [4], soluble and exchangeable potassium levels in soil extracts [14], quantity-intensity relationships [41], and acid-extractable potassium in feldspars [45] have been carried out. As with the CGEs, the NH$_4^+$ interferes with the response of the VKEs to potassium. To some extent, this interference has been reduced by adding formaldehyde to complex the NH$_4^+$ as hexamethylene-tetramine in alkaline solutions [57] but the formaldehyde introduces additional problems [14]. Nevertheless, as stated by Banin and Shaked [4], "the theoretical and technical advantages of this (VKE) method justify further intensive research on this kind of electrode."

Explanation of Dissertation Format

The results of this dissertation are presented in three sections. Section I describes the electrochemical cell requirements and procedures needed to determine potassium in soil extracts. Section II is an
evaluation of ion-selective electrode methods of determining the exchangeable potassium in soil extracts. Section III describes a procedure for the construction of tube-mounted membrane electrodes and presents an evaluation of tube-mounted membrane electrodes with different membrane compositions.

Each section is in the form of a journal article. A portion of the material in Sections I and II was reported at the 1983 meetings of the American Society of Agronomy, while Section III was submitted to Talanta for publication. These sections on the results are preceded by a general introduction and followed by some general conclusions about their significance. References cited in the General Introduction are listed in Additional Literature Cited, which follows the General Discussion. This format is authorized on page 6 of the 1981 edition of the Iowa State University Thesis Manual.
SECTION I. CELL AND PROCEDURE REQUIREMENTS FOR ION-SELECTIVE ELECTRODE DETERMINATIONS OF POTASSIUM
ABSTRACT

Electrochemical cells for the determination of potassium consist of a potassium ion-selective electrode (K-ISE) and a reference electrode that contacts the test solution either directly (i.e., cells without transference) or through a salt bridge (i.e., cells with transference). The choice of both the K-ISE and the reference electrode depends on a number of factors, including the ionic strength and composition of the test solutions and the presence of interfering ions. The performance characteristics of several electrochemical cells have been critically evaluated. Cells without transference were found to be suitable for specific situations where the ion contributing to the potential of the reference electrode can be maintained at a constant level and does not interfere with the K-ISE. A cell consisting of a pH glass electrode, a valinomycin-based K-selective electrode (VKE), and a solution adjusted for ionic strength and pH by lithium chloride and lithium hydroxide-diethylamine, respectively, was well-suited for potassium determinations when NH$_4^+$ interferences were negligible. However, cells with transference were of more general utility. Many of the salt bridges that have been used or recommended for use with K-ISEs in cells with transference gave inaccurate results because the salts did not provide constant or negligible $E_j$ and/or they interacted with the K-ISEs. A sleeve-type double-junction reference electrode with a saturated lithium acetate bridge provided the best results.

Several commercial and laboratory-prepared K-ISEs were evaluated. Ammonium, Na$^+$, and Li$^+$ each posed a serious interference problem with the
cationic glass electrode (CGE) but only NH$_4^+$ presented a serious problem with the neutral carrier-based (valinomycin and dibenzo-18-crown-6) electrodes. Difficulties due to NH$_4^+$ were minimized by titrating the test solutions to pH 11.6-11.8 with lithium hydroxide. In this manner, NH$_4^+$ interferences were reduced by ~98% in solutions containing 10$^{-5}$ M potassium and were eliminated in solutions containing potassium concentrations greater than or equal to 10$^{-3}$ M.
INTRODUCTION

Potassium (K) is one of the macronutrients essential to all living organisms. Ultimately, this potassium must be provided by the soil; therefore, its behavior in soils and availability to plants is of considerable importance. For nearly 30 years, most investigations of potassium chemistry in soils have relied on conventional flame analysis methods for the determination of potassium in extracts. The susceptibility of the extracted potassium to analysis by atomic emission or absorption spectrometric methods has, therefore, been a major factor in the success of this approach. Although these methods are generally quite accurate; spectral, ionization, and matrix interferences \[13,27\] may lead to erroneous or irreproducible results. Moreover, they are not adaptable to in situ analysis or the monitoring of reactions involving potassium. Within the past 25 years, however, advances in ion-selective electrode (ISE) technology \[1,2,14\] have opened up new opportunities for the in situ determination of potassium in extracts and possibly even in microregions of soils and plants.

Several investigators have used cationic glass electrodes (CGEs) as K-ISEs to determine potassium in soil suspensions \[20\], pastes \[15\], and extracts \[10\]. However, the K-selectivity of these electrodes was rather poor and as a result, extractable cations other than potassium (most notably \(\text{Na}^+\), \(\text{NH}_4^+\), and \(\text{H}^+\)) interfered with the potassium determinations. At the same time, Malcolm and Kennedy \[17\] demonstrated the enormous potential of the K-ISEs by using a CGE to determine the rates of potassium exchange on K-saturated clays in suspensions.
One of the most significant advances in ISE technology has been the development of the valinomycin-based K-selective electrodes (VKEs) [4,24]. These electrodes are about 1000-times more selective for $K^+$ over $Na^+$ and $H^+$ and about 100-times more selective for $K^+$ over $NH_4^+$ than the CGEs [2]. As a result, the relatively small amounts of these interfering ions indigenous to most soils should have much less of an effect on the measurement of soil potassium by VKEs. However, interferences from $NH_4^+$ and, to a lesser extent, $Na^+$ in the solutions used to extract the soil potassium (e.g., 1.0 M $NH_4$OAc and 1.0 M NaCl-0.2 M NaTPB) can be a major problem [10].

Electrochemical cells for the determination of any ion consist of an ISE and a reference electrode that: (1) completes an electrical circuit and (2) functions as a half-cell of constant potential against which variations in the potential of the ISE are measured. Obviously, a reproducible reference electrode potential is essential for accurate ion determinations. In most potentiometric methods of analysis this requirement is met by using either a calomel or a silver-silver chloride reference electrode assembly with a 3.5 M or saturated potassium chloride salt bridge [6]. However, leakage of potassium ions from these bridge solutions makes them unsuitable for use with K-ISEs. A variety of alternative salt bridges have been used in conjunction with K-ISEs [3,7,22,25], but their suitability for routine use has not been established.

Although, over the past decade, VKEs and automated analyzers employing VKEs have begun to find widespread use in clinical laboratories [8], only rarely have they been used in soil investigations [3,10,15,
Ultimately, however, it is expected that these electrodes will provide an excellent tool for the routine determination of potassium in soil extracts and may lead to new ways of characterizing the forms, reactions and relevance of potassium in soils and minerals. The purpose of this study was to establish the cell requirements and procedures for the potentiometric determination of potassium under the conditions prevailing in soil extracts. Emphasis was placed on evaluating the various options regarding the selection of a suitable reference electrode and the methods of minimizing NH$_4^+$ interferences.
EXPERIMENTAL

Reagents

Deionized water and chemicals of ACS analytical grade quality were used to prepare all solutions, except lithium trichloroacetate. Saturated solutions of lithium trichloroacetate were obtained from Orion Research Inc., Cambridge, MA.

Electrodes

The potassium-selective electrodes used were the Orion 93-19 (OVKE), Corning 476132 (CVKE), and Lazar ISM-146K (LVKE) valinomycin-based ISEs; a Beckman 39137 cationic glass electrode (BCGE); and two tube-mounted membrane electrodes [11] based on valinomycin (TM-VKE) and dibenzo-18-crown-6 (TM-CKE). These electrodes were stored in $10^{-3}$ M potassium chloride.

A silver-silver chloride electrode [11], a Radiometer G502Na sodium-selective glass electrode (Na-GE), and a Corning 476022 hydrogen-selective glass electrode (H-GE) were used as reference electrodes in cells without transference. In cells with transference, an Orion 90-02 double-junction sleeve-type reference electrode (RE), with various outer salt bridge solutions, was used.

Apparatus and Experimental Techniques

Cell e.m.f. values (E) were measured with a Corning pH/Ion 135 meter equipped with the dual-ISE option, and were recorded when the rate of change was <0.1 mV min$^{-1}$. All measurements were performed at $22 \pm 0.1^\circ C$ in plastic beakers, with the test solutions mixed at constant speed. Calibration measurements were carried out in sequence from dilute to more
concentrated solutions, the electrodes being rinsed with $10^{-6}$ M potassium chloride and lightly blotted dry between measurements. Prior to each complete calibration sequence, the electrodes were soaked in $10^{-6}$ M potassium chloride for 15-20 min.

An Orion 801A digital ionalyzer was used for all pH measurements; the pH values were recorded when the rate of change was $\leq 0.005$ pH min$^{-1}$.

Evaluation of Electrode Behavior

Calibration curves were constructed by plotting $E$(mV) vs. $-\log a_{K^+}$ (or $-\log c_{K^+}$). Activity coefficients were calculated using the extended Debye-Huckel equation [16]. The slopes of the calibration curves were calculated by means of regression analysis on the linear (i.e., $r \geq 0.9998$) part of the curves. The lower limit of linear response (LLLR) was defined as the potassium ion activity (concentration) at the point of intersection of the regression line and the nonlinear portion of the calibration curve. The limits of detection (LD) were determined using the statistical methods discussed by Midgley [18]. Potentiometric selectivity coefficients ($k_{Pot}^{K^+}$) were determined using the fixed interference method [2,5].
RESULTS AND DISCUSSION

Reference Electrodes

Aside from interferences at the K-ISE, the liquid junction between the reference electrode and the test solution may be the biggest source of error associated with potassium determinations by K-ISEs. One solution to the problems and uncertainties associated with liquid junctions [6] is to avoid them by using a second ISE as the reference electrode, provided it is unaffected by the determinand (i.e., K⁺). Most ISEs, however, have too high an impedance (≥10⁹Ω) for the reference electrode input (≤10⁴Ω impedance) of most pH/Ion meters. Thus, the reference-ISE must be selected for its low impedance or a special pH/Ion meter with two high impedance inputs must be used. Furthermore, the activity of the ion that determines the reference-ISE potential must be maintained at a constant level. In soil extracts, this condition may be met by the extracting solution itself.

With this in mind, a Na-selective glass electrode (Na-GE; cation-sensitive with a high impedance) and a Cl-selective silver halide electrode (Ag,AgCl; anion-sensitive with a low impedance) were evaluated as reference-ISEs.

Calibration curves for the cells:

\[ \text{Ag,AgCl/NaCl (0.1 M), KOAc (xM)/OKE} \] (cell IA)

\[ \text{Na-GE/NaCl (0.1 M), KOAc (xM)/OKE} \] (cell IIA)

are shown in Figure 1. The cell e.m.f. (E) can be expressed by a modification of the Nicolsky equation as

\[ E = E^0 + 58.6 \log \left[ \left( a_{K^+} \right) + \left( c_{K^+} + k_{Na^+} \cdot a_{Na^+} \right) \right] \] (1)
Figure 1. Calibration results obtained with the Orion K-selective electrode (OVKE) versus Cl-selective (Ag,AgCl) and Na-selective (Na-GE) reference electrodes at constant ionic strength.
where $E^0'$ is a cell constant consisting of the cell e.m.f. when $a_{K^+} = 1$ and includes the potentials of the internal and external reference electrodes and the asymmetry potentials; 58.6 is the slope factor at 22°C; $a_{K^+}$ and $a_{Na^+}$ are the potassium and sodium ion activities, respectively; $c_{Ki}$ is the concentration of potassium introduced as an impurity in the sodium chloride ionic strength adjustor (ISA); and $k_{Pot}^{KNa}$ is the selectivity coefficient (for the OVKE) for $K^+$ over $Na^+$. When the potassium ion activity is very low the cell e.m.f. is determined chiefly by the contribution of the sodium chloride (i.e., $c_{Ki} + k_{Pot}^{KNa} \cdot a_{Na^+}$) to the total measurable activity. As the potassium ion activity increases, however, the relative contribution of the sodium chloride to the total measurable activity decreases and equation (1) reduces to

$$E = E^0' + 58.6 \log a_{K^+}$$

i.e., the Nernst equation. The minimum potassium ion activity at which the Nernst equation applies is referred to as the lower limit of linear response (LLLR). The limit of detection (LD) is defined on a statistical basis as the activity at which there is a 5% chance of failing to detect potassium [18].

In addition to the use of sodium extracting solutions, it was anticipated that potassium determinations in soil extracts would also involve the use of pH control to reduce $NH_4^+$ interferences. Thus, a glass pH electrode (H-GE) was also evaluated as a reference-ISE.

The calibration data obtained with cells employing Cl-, Na-, and H-ISEs as reference electrodes, the OVKE, and various ionic strength and
pH adjustors are summarized in Table 1. All the cells exhibit near-Nernstian slopes (i.e., within 5% of the theoretical value) and have an upper limit of linear response near pH 1. For cells with a common reference-ISE, the variations in the LLLR and LD are due to differences in the selectivity of the OVKE for the cations of the ionic strength and pH adjusters (i.e., Na$^+$, Li$^+$, H$^+$, and DEA$^+$). The differences between cells IA and IIA, on the other hand, are presumably due to varying amounts of potassium impurities in the sodium chloride, which were prepared from different sources.

These results verify the suitability of using cells without transference for potassium determinations in systems that maintain a constant level of the reference-ISE potential-determining ion. However, this requirement that the ionic strength of the test solutions remain constant is also the optimum condition for minimizing the liquid junction effect in the more conventional cells with transference. Consequently, unless activity ratios or products are being sought, if this condition exists there are few advantages in using an ISE as the reference electrode.

Commercial reference electrode assemblies are much cheaper than ISEs; they have low impedances and, thus, can be used with any pH/Ion meter; and a single electrode assembly can be adapted to a wide variety of solution conditions. Therefore, provided that a suitable salt bridge solution is available, cells with transference are nearly always used in routine analytical work. Salt bridge solutions commonly employed in the potentiometric determination of potassium ion activities (concentrations) include concentrated solutions of lithium trichloroacetate [2,3], lithium acetate
Table 1. Experimentally determined response characteristics of the Orion K-selective electrode (OVKE) in cells without transference.

<table>
<thead>
<tr>
<th>Electrochemical cell</th>
<th>Slope^a^ (mV/pK^+^)</th>
<th>LLLR^b^ (µM K^-)</th>
<th>LD^b^ (µM K^-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IA. Ag,AgCl/0.1M NaCl,xM KOAc/OVKE</td>
<td>58.7</td>
<td>40 a</td>
<td>4.8 a</td>
</tr>
<tr>
<td>IB. Ag,AgCl/0.1M LiCl,xM KOAc/OVKE</td>
<td>58.7</td>
<td>6.4 b</td>
<td>1.1 bc</td>
</tr>
<tr>
<td>IIA. Na-GE/0.1M NaCl,xM KCl/OVKE</td>
<td>56.7</td>
<td>46 c</td>
<td>6.6 d</td>
</tr>
<tr>
<td>IIB. Na-GE/0.1M LiCl,xM KCl/OVKE</td>
<td>57.2</td>
<td>7.6 b</td>
<td>1.6 b</td>
</tr>
<tr>
<td>IIIA. H-GE/HOAc-LiOH(^c),0.1M LiCl,xM KCl/OVKE</td>
<td>57.5</td>
<td>24 d</td>
<td>2.9 e</td>
</tr>
<tr>
<td>IIIB. H-GE/HOAc-DEA(^d),0.1M LiCl,xM KCl/OVKE</td>
<td>57.2</td>
<td>8.4 b</td>
<td>1.0 bc</td>
</tr>
<tr>
<td>IIIC. H-GE/0.006M LiOH(^e),0.1M LiCl,xM KCl/OVKE</td>
<td>57.2</td>
<td>6.4 b</td>
<td>0.64 c</td>
</tr>
</tbody>
</table>

^a^Theoretical slope = 58.6 mV/pK^+^.

^b^Within columns, means (n=2) followed by the same letter are not significantly different at the 5% level, by Duncan's Multiple Range Test.

^c^0.001M HOAc - 0.0005M LiOH, solution buffered at pH 4.8.

^d^0.0285M HOAc - 0.102M diethylamine, solution buffered at pH 11.6.

^e^Solution adjusted to pH 11.6 with 1.0M LiOH.

[15], sodium chloride [7], and ammonium nitrate [25]. The relative merits of these bridge solutions, however, have not been established and none has been universally accepted. Thus, these bridge solutions, and one of concentrated lithium chloride, were evaluated to determine which of them is best suited for use with K-ISEs.

The stability and reproducibility of the reference electrode potential depends on the configuration of the liquid junction as well as on the composition of the bridge solution [6,9]. Reference electrode assemblies
with a number of different junction configurations are commercially available. But, to avoid many of the problems associated with liquid-junction potentials, renewable ground-joint (sleeve-type) junctions should be used [6]. This type of junction provides (for a given bridge solution) a low liquid-junction potential for most samples, is easily cleaned, and is the "closest junction to being universal" [29].

The different bridge solutions were evaluated using a sleeve-type double-junction reference electrode assembly. The general cell arrangement was

\[ \text{Ag,AgCl} / \text{bridge soln} / \text{ISA(1 M),KCl(xM)}/0VKE \text{ (cell IV)} \]

\[ E_{\text{Ag,AgCl}} = E_{j1} + E_{j2} \]

where the reference solution is an equitransferent solution (Orion 90-00-02; 1.70 M KNO\textsubscript{3} + 0.64 M KCl + 0.06 M NaCl + 1 ml L\textsuperscript{-1} 37% HCHO), and saturated with silver chloride) that provides for a specific \( E_{\text{Ag,AgCl}} \).

For a given bridge solution, the liquid-junction potential \( E_{j1} \) is a constant. The liquid-junction potential \( E_{j2} \), on the other hand, may vary considerably as the composition and ionic strength of the test solutions change. In general, the measured e.m.f. (E) of cell IV can be expressed by modifying equation (1) to include the liquid junction potentials. Thus,

\[ E = E^{0'} + 58.6 \log \left[ (a_{K^+}) + (c_{K^+} + k_{K^+}^{\text{Pot}} \cdot a_x^{1/z_x}) \right] - E_{j2} \]  

where \( E^{0'} \) is the cell constant including \( E_{j1} \); \( a_x \) and \( z_x \) are the activity and valence of the ISA cation, respectively; and \( k_{K^+}^{\text{Pot}} \) is the generalized selectivity coefficient. Accurate potentiometric determinations of
potassium ion activity (concentration) require that $E_{j2}$ be negligible or, at the very least, remain relatively constant as the composition of the test solution varies. This may be accomplished either by using a concentrated bridge solution of a salt whose ions have approximately equal transference numbers or by adding an excess of a supposedly inert electrolyte (i.e., ISA) to the test solutions so that their ionic strength and composition remain constant. Moreover, by choosing a bridge solution having essentially the same ionic strength and composition as the test solution (e.g., bridge solution = ISA) $E_{j2}$ can be expected to be approximately zero.

Calibration data obtained with cell IV using bridge solutions of 1.2 M ammonium nitrate, saturated lithium trichloroacetate or lithium acetate, and 2.0 M sodium or lithium chloride are summarized in Table 2. In the absence of any ISA, the cells employing nearly-equitransferent bridge solutions (i.e., ammonium nitrate, lithium trichloroacetate and lithium acetate) exhibit near-Nernstian slopes. The LLLRs and LDs are low and not significantly different indicating that junction potential effects are small. The cells employing nonequitransferent bridge solutions (i.e., sodium chloride and lithium chloride), on the other hand, exhibit super-Nernstian slopes and significantly higher LLLRs and LDs. These responses are due to relatively large junction potentials that vary with the ionic strength (i.e., potassium chloride concentration) of the calibration standards. Nernst originally suggested that by adding an excess of an inert electrolyte to both the bridge and test solutions so that they had essentially the same ionic strength and composition the liquid-junction
Table 2. Effect of salt bridge solutions and ionic strength adjustments on the experimentally determined response characteristics of the Orion K-selective electrode (OVKE) in cells with transference

<table>
<thead>
<tr>
<th>Cell</th>
<th>Salt bridge</th>
<th>ISA</th>
<th>$1^a$ (M)</th>
<th>Slope $^b$ (mV/pK$^+$)</th>
<th>LLR</th>
<th>LD $^c$ (µM K$^{+}$)</th>
<th>LD $^c$ (µM K$^{+}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IVA</td>
<td>1.2 M NH$_4$NO$_3$</td>
<td>LiNO$_3$</td>
<td>0.0</td>
<td>57.4</td>
<td>58.1</td>
<td>2.9</td>
<td>0.49</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.1</td>
<td>58.0 ns $^d$</td>
<td>4.8</td>
<td>0.86</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.0</td>
<td>55.6 ns</td>
<td>45</td>
<td>6.2</td>
<td></td>
</tr>
<tr>
<td>IVB</td>
<td>sat'd LiCl$_3$OAc</td>
<td>LiOAc</td>
<td>0.0</td>
<td>59.0</td>
<td>58.2</td>
<td>3.0</td>
<td>0.62</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.1</td>
<td>58.1 ns</td>
<td>4.4</td>
<td>0.74</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.0</td>
<td>58.0 ns</td>
<td>43</td>
<td>5.2</td>
<td></td>
</tr>
<tr>
<td>IVC</td>
<td>sat'd LiOAc</td>
<td>LiOAc</td>
<td>0.0</td>
<td>59.9</td>
<td>58.7</td>
<td>2.5</td>
<td>0.50</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.1</td>
<td>58.6 ns</td>
<td>4.1</td>
<td>0.84</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.0</td>
<td>58.4 ns</td>
<td>39</td>
<td>4.8</td>
<td></td>
</tr>
<tr>
<td>IVD</td>
<td>2.0 M NaCl</td>
<td>NaCl</td>
<td>0.0</td>
<td>70.1</td>
<td>58.0</td>
<td>40</td>
<td>2.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.1</td>
<td>58.8 58.0</td>
<td>98</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.0</td>
<td>56.6 ns</td>
<td>540</td>
<td>74</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2.0</td>
<td>54.9 ns</td>
<td>1200</td>
<td>120</td>
<td></td>
</tr>
<tr>
<td>IVE</td>
<td>2.0 M LiCl</td>
<td>LiCl</td>
<td>0.0</td>
<td>78.4</td>
<td>58.1</td>
<td>44</td>
<td>4.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.1</td>
<td>59.2 58.0</td>
<td>6.2</td>
<td>0.96</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.0</td>
<td>57.8 ns</td>
<td>43</td>
<td>7.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2.0</td>
<td>56.8 ns</td>
<td>120</td>
<td>14</td>
<td></td>
</tr>
<tr>
<td>LSD</td>
<td>$^{(a=0.05)}$</td>
<td></td>
<td>0.4</td>
<td>4.7</td>
<td>0.33</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ I = molar concentration of the ISA in the test solutions.
$^b$ Slope of the calibration curves between the LLR and 0.1 M KCl.
$^c$ Expt’l slope minus the estimated $E_{j2}$ (Henderson's approximation).
$^d$ No significant difference between expt’l and calc’d slopes.
potential could be reduced to approximately zero [6]. The data presented in Table 2 and Figure 2, however, show that at high ionic strengths interferences from the ISA/bridge cation can be a more serious problem than the liquid-junction potential effects. On the other hand, at low ionic strengths it has been shown that the liquid-junction potential is very sensitive to changes in the composition and ionic strength of the test solutions [12]. A more useful approach is to use a concentrated bridge solution (so that it dominates the junction) and add just enough ISA to the test solutions so that their total ionic strength remains constant and variations in $E_j^2$ become small. In general, increasing the concentration of the ISA reduces the junction potential effects (i.e., $\Delta E_j^2/\Delta pK^+$) and increases the LLLRs and LDs. Variations in the LLLRs and LDs are due to differences in the selectivities of the OVKE for potassium over lithium and sodium ($k_{KL} = 10^{-5}$, $k_{KNa} = 10^{-4}$) and varying amounts of potassium impurities in the ISAs (e.g., $c_{K_i} = 20 \mu \text{M}$ in 1.0 M NaCl and only $\sim 1 \mu \text{M}$ in 1.0 M LiCl; determined by AAS).

The stabilities and reproducibilities of the liquid junction potentials were determined using the cell

$$\text{RE} // \text{bridge soln} // \text{KCl} (x \text{M}\AgCl \text{sat'd})/\AgCl,\Ag \quad \text{(cell V)}$$

where RE is the double-junction reference electrode assembly. The cell e.m.f. is given by the equation

$$E = (E^{0}_{\Ag,\AgCl} - 58.6 \log a_{Cl^-}) - (E_{RE} + E_{j2}) \quad (4)$$

$$E = \text{constant} - E_{j2} \quad (4a)$$
Figure 2. Calibration results obtained with the Orion K-selective electrode (OVKE) versus the sleeve-type double-junction reference electrode with saturated LiOAc (C) and 2.0 M NaCl (D) salt bridges and test solutions that had different ionic strengths.
thus, any change in the cell e.m.f. is attributable to the liquid junction potential $E_{j_2}$. The silver-silver chloride electrode was pre-equilibrated in the potassium chloride test solution to insure that any change in the cell e.m.f. was due only to a change in $E_{j_2}$. Figure 3 illustrates the drift in $E_{j_2}$ (as measured by a change in the cell e.m.f.) in $10^{-5}$ M potassium chloride as a function of time. In general, $E_{j_2}$ drifts at a rate of $\pm 0.15 \text{ mV min}^{-1}$ during the first 10 minutes, then at rates of about $+0.01$, $-0.02$, and $+0.04 \text{ mV min}^{-1}$ over the next 50 minutes when the bridge solutions are lithium acetate, ammonium nitrate, and lithium trichloroacetate, respectively. Most of the rapid initial change in $E_{j_2}$ is probably due to the establishment of the junction, whereas the later changes are due to increasing charge separation, i.e., the unequal mobilities of the bridge ions. The reproducibilities of the liquid-junction potentials were poor (+2 mV) during the first 5 minutes but improved with time (+0.4 mV after 15 minutes). Increasing the ionic strength (or potassium chloride concentration) of the test solutions to $\sim 10^{-3}$ M increased both the stability ($\Delta E_{j_2} < 0.01 \text{ mV min}^{-1}$ in 3-5 minutes) and reproducibility (+0.2 mV) of $E_{j_2}$. At all concentrations of potassium chloride ($10^{-6}$ - $10^{-2}$ M) the drift in $E_{j_2}$ was within tolerable limits ($< 0.10 \text{ mV min}^{-1}$) in 5-10 minutes. And, as shown in Table 2, reproducible potassium determinations can be obtained by using a drift rate of $< 0.1 \text{ mV min}^{-1}$ as the criterion for a "stable" e.m.f. value.

Contamination of the test solution by ions moving out of the salt bridge occurs to varying degrees whenever cells with transference are used and may be a source of significant error if the potassium concentrations
Figure 3. Change of $E$ with time for the cell: RE/bridge soln/KCl 
($10^{-5}$ M, AgCl sat'd)/AgCl,Ag, with different bridge solutions
are low. Figure 4 shows the effect that leakage of different bridge solutions can have on the responses of the BCGE and OVKE in $10^{-5}$ M potassium chloride. Neither lithium acetate nor lithium trichloroacetate have much of an effect on the BCGE and relatively stable potentials (i.e., $\Delta E < 0.1 \text{ mV min}^{-1}$) were reached in about 5-7 minutes. The use of ammonium nitrate, on the other hand, produced significant contamination because of the poor selectivity of the BCGE for $K^+$ over $NH_4^+$ ($k_{Pot}^{Pot} = 0.15$). The situation is entirely different with the OVKE. Here, lithium acetate and ammonium nitrate present relatively minor problems, whereas, lithium trichloroacetate poses a significant problem. The response of the OVKE to the bridge cation accounts for nearly all the drift when ammonium nitrate is the bridge solution ($k_{Pot}^{Pot} = 0.01$), but cannot account for any of the drift when lithium trichloroacetate and lithium acetate bridge solutions are used. Thus, it is believed that the trichloroacetate anion is the cause of the problem. Further investigation showed the effects of lithium trichloroacetate contamination to be dependent upon the potassium ion concentration and the total ionic strength of the test solution, decreasing as either increased.

Based on these results, it was concluded that for routine potentiometric determinations of potassium, the most suitable reference half-cell consists of a sleeve-type double-junction reference electrode assembly with a saturated lithium acetate bridge solution. This half-cell was used throughout the remainder of this study.

As has already been discussed, the addition of an ISA to the test solutions can (1) reduce the liquid-junction potential effects, (2)
Figure 4. Change of $E$ with time showing the effects of contamination by ions leaking from different salt bridges on the response of the Beckman cationic glass electrode (BCGE) and the Orion K-selective electrode (OVKE) in 100 ml of $10^{-5}$ M KCl.
decrease the time needed to reach a stable potential, and (3) reduce contamination from bridge solution. In addition, ISAs are routinely used to fix the activity coefficient of the determinand so that the measured cell e.m.f.s can be directly related to ion concentrations rather than activities. Sodium salts are usually recommended as ISAs when potassium is to be determined potentiometrically, however, the data in Tables 1 and 2 indicate that lithium salts would be a better choice. However, potassium impurities on ISAs must also be considered. The effects of different ISAs on the response characteristics of cell IVC are illustrated in Table 3. The data show that, in general, lithium salts have less of an effect than barium or sodium salts and that for a given cation interference increases in the order acetate < nitrate < chloride. Flame analysis of these salts showed that potassium impurities increased in the same order. As a result, it is recommended that 0.1 M lithium acetate should be used as the ISA when K-ISEs are used.

**Comparison of K-ISEs**

The response characteristics of several commercially available and laboratory-prepared K-ISEs are summarized in Table 4. The selectivities of the K-ISEs were determined in mixed solutions containing constant concentrations of interferent, added as the acetates, and potassium ion concentrations ranging from $10^{-7}$ to $10^{-2}$ M. The selectivity coefficients were calculated using the equation

$$k_{\text{Pot}} = \frac{a^+_K}{a_X} \left(\frac{1}{z_X}\right)$$

(5)
Table 3. Experimentally determined response characteristics of the Orion K-selective electrode (OVKE) versus the sleeve-type double-junction reference electrode with a saturated LiOAc salt bridge as affected by different ionic strength adjusters (ISAs)

<table>
<thead>
<tr>
<th>ISA</th>
<th>( I^a ) (M)</th>
<th>Slope(^b) (mV/pK(^+))</th>
<th>LLLR(^b) (( \mu M ) K(^+))</th>
<th>LD(^b) (( \mu M ) K(^+))</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>---</td>
<td>58.8 a</td>
<td>2.5 a</td>
<td>0.50 a</td>
</tr>
<tr>
<td>NaOAc</td>
<td>0.1</td>
<td>57.4 b</td>
<td>6.8 b</td>
<td>1.2 b</td>
</tr>
<tr>
<td>NaNO(_3)</td>
<td>0.1</td>
<td>57.2 b</td>
<td>10 c</td>
<td>1.6 c</td>
</tr>
<tr>
<td>NaCl</td>
<td>0.1</td>
<td>57.8 b</td>
<td>32 d</td>
<td>3.1 d</td>
</tr>
<tr>
<td>LiOAc</td>
<td>0.1</td>
<td>58.6 a</td>
<td>4.1 a</td>
<td>0.84 ab</td>
</tr>
<tr>
<td>LiNO(_3)</td>
<td>0.1</td>
<td>58.4 a</td>
<td>4.8 a</td>
<td>0.86 ab</td>
</tr>
<tr>
<td>LiCl</td>
<td>0.1</td>
<td>58.6 a</td>
<td>6.8 b</td>
<td>1.0 b</td>
</tr>
<tr>
<td>BaOAc(_2)</td>
<td>0.1</td>
<td>57.8 b</td>
<td>4.0 a</td>
<td>0.67 a</td>
</tr>
<tr>
<td>BaCl(_2)</td>
<td>0.1</td>
<td>57.7 b</td>
<td>53 e</td>
<td>5.7 e</td>
</tr>
</tbody>
</table>

\(^a\) I = Molar concentration of the ISA in the test solutions.

\(^b\) Within columns, means (n=2) followed by the same letter are not significantly different at the 5% level, by Duncan's Multiple Range Test.

where \( a_K^+ \) is the potassium ion activity at the point where the experimental calibration curve deviates from the regression line by \( \approx 18 \) mV [2].

Although the K-ISEs are known to respond in varying degrees to most of the alkali and alkaline earth cations [2,19] only sodium, barium, and ammonium are considered to pose potential problems in soil and mineral analyses. The data in Table 4 show that ammonium, sodium, and lithium each pose a serious interference problem with the cationic glass electrode (No. 7) while only ammonium presents a major interference problem with the neutral carrier based electrodes (No. 1-6). Furthermore, electrodes 1-6 exhibit no hydrogen ion interference as long as \( pH \geq pK^+ \). It is expected that the
Table 4. Experimentally determined response characteristics of various K-selective electrodes versus the sleeve-type double-junction reference electrode with a saturated LiOAc salt bridge.

<table>
<thead>
<tr>
<th>K-ISE Designation</th>
<th>Slope&lt;sup&gt;a&lt;/sup&gt; (mV/pK&lt;sup&gt;a&lt;/sup&gt;)</th>
<th>LLLR&lt;sup&gt;a&lt;/sup&gt; (μM K&lt;sup&gt;a&lt;/sup&gt;)</th>
<th>LD&lt;sup&gt;a&lt;/sup&gt; (μM K&lt;sup&gt;a&lt;/sup&gt;)</th>
<th>-log&lt;sup&gt;b&lt;/sup&gt; k&lt;sub&gt;KX&lt;/sub&gt;&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Pot&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Na&lt;sup&gt;+&lt;/sup&gt;</th>
<th>NH&lt;sub&gt;4&lt;/sub&gt;&lt;sup&gt;+&lt;/sup&gt;</th>
<th>Li&lt;sup&gt;+&lt;/sup&gt;</th>
<th>Ba&lt;sup&gt;2+&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 OVKE</td>
<td>59.0 a</td>
<td>2.4 a</td>
<td>0.46 a</td>
<td>3.97 a</td>
<td>1.80 a</td>
<td>4.99 a</td>
<td>4.90 a</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 OVKE(A)</td>
<td>59.2 a</td>
<td>1.1 b</td>
<td>0.19 b</td>
<td>4.71 b</td>
<td>2.02 a</td>
<td>5.38 b</td>
<td>4.74 b</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 CVKE</td>
<td>59.3 a</td>
<td>1.8 b</td>
<td>0.22 b</td>
<td>4.66 b</td>
<td>1.95 a</td>
<td>5.02 a</td>
<td>4.99 a</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4 LVKE</td>
<td>59.3 a</td>
<td>0.29 c</td>
<td>0.058 c</td>
<td>4.83 b</td>
<td>2.01 a</td>
<td>5.22 ab</td>
<td>4.72 b</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 TM-VKE</td>
<td>59.1 a</td>
<td>0.56 c</td>
<td>0.083 c</td>
<td>4.95 c</td>
<td>1.96 a</td>
<td>5.32 b</td>
<td>5.45 c</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6 TM-CVE</td>
<td>59.2 a</td>
<td>0.56 c</td>
<td>0.12 bc</td>
<td>4.78 bc</td>
<td>2.02 a</td>
<td>5.35 b</td>
<td>4.72 b</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7 BCGE</td>
<td>58.3 b</td>
<td>27 d</td>
<td>3.3 d</td>
<td>1.16 d</td>
<td>0.85 b</td>
<td>2.42 c</td>
<td>4.19 b</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup>Within columns, means (n=4) followed by the same letter are not significantly different at the 5% level, by Duncan's Multiple Range Test.

<sup>b</sup>X is Na<sup>+</sup>(0.10 M), NH<sub>4</sub><sup>+</sup> (0.01 M), Li<sup>+</sup> (0.10 M), or Ba<sup>2+</sup> (0.10 M) for the neutral carrier-based electrodes (No. 1-6) and Na<sup>+</sup> (0.010 M), NH<sub>4</sub><sup>+</sup> (0.001 M), Li<sup>+</sup> (0.010 M), or Ba<sup>2+</sup> (0.010 M) for the cationic glass electrode (No. 7).

The response characteristics of the VKEs changed with the age of the K-selective membranes. Electrodes 2, 4, and 5 had been used for only 7-10 days when their calibration data were obtained, whereas, electrodes 3 and 1 had been in use for 1 and 2 years, respectively. Fresh electrodes are obviously the best for determinations of very low potassium levels. A comparison of the tube-mounted membrane electrodes incorporating valinomycin (No. 5) and dibenzo-18-crown-6 (No. 6) shows there was no significant differences in their response characteristics except for barium selectivity. This difference is not enough, however, to rule out the use of ammonium problem can be overcome, thus making the potentiometric determination of potassium in soil extracts feasible.
of TM-CKE with barium solutions. Moreover, the response characteristics of these electrodes remained practically constant for a four-month period.

Ammonium Ion Interference

Figure 5 shows the calibration curves obtained in mixed potassium chloride-ammonium acetate solutions where the potassium ion concentration \( (c_K^+) \) was varied at constant ammonium ion concentrations \( (c_{NH_4}^+) \). In general, the selectivity coefficient remains constant and at potassium ion concentrations greater than or equal to \( 10^{-5} \) M, ammonium ion interference is significant only when \( c_{NH_4}^+ > 5 c_K^+ \). However, at lower potassium ion concentrations, the selectivity coefficient increases and at \( 10^{-6} \) M potassium chloride interference becomes significant when \( c_{NH_4}^+ > 2 c_K^+ \).

It should be possible to control ammonium ion interference by controlling the reaction

\[
\text{NH}_4^+ (aq) + \text{OH}^- (aq) \rightleftharpoons \text{NH}_3 (g) + \text{H}_2\text{O} , \quad \text{pK}_a = 9.2
\]

because the VKEs are not sensitive to \( \text{NH}_3 (g) \). The high selectivity of the VKEs for potassium over lithium (Table 4) and the high pHs attainable with lithium hydroxide make this base an ideal source of hydroxyl ions for this reaction. Moreover, an analysis of the lithium hydroxide detected only minor amounts of potassium impurities \( (c_{K_i} = 7 \mu\text{M} \text{ in } 1.0 \text{ M LiOH}) \). Thus, lithium hydroxide was used to study the effects of increasing pH on NH\(^+\) interference (Figure 6). Curve 1A shows the change in E that occurred when a \( 10^{-5} \) M potassium chloride - 0.10 M ammonium acetate solution was titrated with 2.0 M lithium hydroxide. The NH\(^+\) interference was reduced \( \approx 98\% \) by increasing the pH to \( \approx 12 \) (5.25 ml LiOH). At this pH, only about
Figure 5. Calibration results obtained with the Corning K-selective electrode (CVKE) in solutions containing fixed levels of NH₄OAc and varying concentrations of KCl, at pH 6.5
Figure 6. Titration curves showing the effects of additions of 2.0 M LiOH, 2.0 M HCl and 1.8 M LiOH - 2.7 M HCHO on the response of the Corning K-selective electrode in 10^{-5} M KCl - 0.1 M NH_4OAc solutions
0.16% of the ammonium should have been in the cationic form (i.e., $c_{\text{NH}^+} = 1.6 \times 10^{-4} \text{ M}$), this is not enough ammonium to account for more than half the remaining interference.

Increasing the pH further yields no reduction in the interference and actually produces a slight increase in the cell e.m.f. (personal communication with Warren Averill, Corning Medical, Corning Glass Works, Medfield, MA, indicated that there is a pH effect on the VKE at pH $\geq 12$). Curve IB shows the change in E when the test solution was back-titrated with 2.0 M hydrochloric acid. From the increase in E it is evident that most of the ammonium persisted as dissolved ammonia gas in the LiOH-treated solution. As a result, the reaction did not go to completion. Indeed, calculations based on the Nicolsky equation show $\approx 0.35\%$ of the NH$_4^+$ was present.

Attempts to further reduce ammonium ion interference were made by titrating potassium-ammonium solutions with a lithium hydroxide-formaldehyde solution. The reaction between formaldehyde and NH$_4^+$ is described by the equation

$$6 \text{ HCHO (aq)} + 4 \text{ NH}_4^+ \text{ (aq)} + 4 \text{ OH}^- \text{ (aq)} \rightarrow \text{(CH}_2\text{)_6N}_4 \text{ (aq)} + 10 \text{ H}_2\text{O}$$

which has been reported to be quantitative at pH $\geq 9$ [28]. Curve 2 in Figure 6 shows the change in E that was recorded when a $10^{-5} \text{ M}$ potassium chloride-0.10 M ammonium acetate solution was titrated with 1.8 M lithium hydroxide-2.7 M formaldehyde. These data show that the lithium hydroxide-formaldehyde treatment was slightly more effective in reducing the NH$_4^+$ interference but did not eliminate the problem. At the same time, this approach introduced additional problems from the large volumes of
LiOH that had to be added to cope with the release of protons. Also, it has been observed that excess formaldehyde can interfere with the response of K-ISEs [10].

At a given pH, the percentage of NH$_4^+$ remaining as the cation is constant regardless of the initial ammonium ion concentration. Thus, the NH$_4^+$ concentration remaining after pH adjustment is dependent upon the initial NH$_4^+$ concentration. The data in Figure 7 illustrate the effectiveness of pH in reducing ammonium ion interferences at various levels of potassium and ammonium. These data show that the pH corresponding to the maximum reduction of NH$_4^+$ interference increases with decreasing K$^+$ concentration and increasing NH$_4^+$ concentration, and that there is no one optimum pH for maximum reduction of the NH$_4^+$ interference. Since pH levels over 11.8 to 12 are detrimental to VKEs, pH levels of 11.6-11.8 appear to be the best choice for the reduction of NH$_4^+$ problems. If the potassium determinations are carried out at pH 11.8 to minimize NH$_4^+$ interferences, it should be possible to use a pH electrode as the reference electrode. A comparison of this approach versus the more common use of a cell with transference is presented in Table 5 for the cells:

H-GE/0.1 M Li$^+$ (OAc$^- +$ OH$^-$; pH 11.75±0.05), NH$_4$OAc (xM), KCl (yM)/CVKE (cell VI)

RE//sat'd LiOAc//0.1 M Li$^+$ (OAc$^- +$ OH$^-$; pH 11.75±0.05), NH$_4$OAc (xM), KCl (yM)/CVKE (cell VII)

In general, the response characteristics of the two cells were not significantly different, although the reproducibility of the cell e.m.f. at any given K$^+$ concentration was higher for cell VII. However, the calibra-
Figure 7. Titration curves showing the effects of pH on the response of the Corning K-selective electrode in solutions containing varying levels of KCl and NH₄OAc.
Table 5. Experimentally determined response characteristics of the Corning K-selective electrode (CVKE) versus an H-selective reference electrode (cell VI) and a sleeve-type double-junction reference electrode with a saturated LiOAc salt bridge (cell VII) at different levels of NH$_4$OAc and different pH

<table>
<thead>
<tr>
<th>NH$_4$OAc (M)</th>
<th>pH</th>
<th>Cell VI</th>
<th>Cell VII</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Slope (mV/pK$^+$)</td>
<td>LLLR (mg K$^+$L$^{-1}$)</td>
</tr>
<tr>
<td>0.000</td>
<td>7.5</td>
<td>55.6</td>
<td>$\leq 0.2$</td>
</tr>
<tr>
<td>0.000</td>
<td>11.8</td>
<td>56.2</td>
<td>$\leq 0.2$</td>
</tr>
<tr>
<td>0.001</td>
<td>11.8</td>
<td>56.6</td>
<td>$\leq 0.2$</td>
</tr>
<tr>
<td>0.010</td>
<td>11.8</td>
<td>56.3</td>
<td>0.4</td>
</tr>
<tr>
<td>0.100</td>
<td>11.8</td>
<td>56.2</td>
<td>2.5</td>
</tr>
</tbody>
</table>

$^a$Coefficient of variation in the cell e.m.f. (n=5).
Figure 8. Calibration results obtained with the Corning K-selective electrode (CVKE) versus an H-selective reference electrode in solutions at constant pH (11.8) and ionic strength (0.1 M) but different NH₄⁺ concentrations.
Figure 9. Calibration results obtained with the Corning K-selective electrode (CVKE) versus a sleeve-type double-junction reference electrode with a saturated LiOAc salt bridge in solutions at constant pH (11.8) and ionic strength (0.1 M) but different $\text{NH}_4^+$ concentrations.
tion curves for cells VI and VII (Figures 8 and 9, respectively) show that cell VI was sensitive to changes in the $\text{NH}_4^+$ concentration at all $K^+$ levels. On the other hand, at $K^+$ concentrations greater than 1.5 mg K L$^{-1}$ increasing the $\text{NH}_4^+$ concentration had no significant effect on the e.m.f. of cell VII. And, at lower $K^+$ concentrations, only when the initial $\text{NH}_4^+$ concentration was 0.100 M was there any significant interference.

In light of these results, it was concluded that for routine potentiometric determinations of potassium the most suitable reference half-cell is a double-junction reference electrode with a saturated lithium acetate bridge solution. Moreover, $\text{NH}_4^+$ concentrations in solutions representative of soil extracts can be reduced by as much as 98% by titrating the solutions to pH 11.8 with lithium hydroxide, thus, significantly diminishing the severity of ammonium ion interferences with the response of the VKEs to potassium and making potassium determinations in their extracts a possibility.
LITERATURE CITED


SECTION II. AN EVALUATION OF ION-SELECTIVE ELECTRODE METHODS OF DETERMINING EXCHANGEABLE POTASSIUM IN SOILS
ABSTRACT

Procedures using ion-selective electrodes (ISEs) for the accurate determination of \( \text{NH}_4^- \) and \( \text{Ba} \)-exchangeable potassium in soil extracts are described. The exchangeable potassium in 30 soil samples was extracted with neutral solutions of 1.0 M ammonium acetate and 0.5 M barium chloride and determined by atomic absorption spectrometry (AAS) to establish the potassium levels sought with the ISEs. Potentiometric measurements were then made with electrochemical cells consisting of either a valinomycin-based K-selective electrode (VKE) or a cationic glass-membrane electrode (CGE) and a double-junction sleeve-type reference electrode employing a saturated lithium acetate salt bridge. The electrochemically analyzed solutions (1:5 extract-water dilutions) had a common ionic strength and a pH near 7 or a lithium hydroxide adjusted pH of 11.6.

Interferences from ammonium and lithium ions limited the use of the CGE to neutral barium chloride extracts, where it yielded potassium values that were only poorly correlated with those obtained by AAS (\( r=0.655 \)). However, the \( \text{Ba} \)-exchangeable potassium values obtained by AAS were highly correlated (\( r=0.983 \)) with and not significantly different (\( \alpha=0.05 \)) from those obtained with the VKE in the neutral extracts and even more so in the solutions at pH 11.6 (\( r=0.998; \alpha=0.01 \)). In addition, a comparison of the AAS values for the \( \text{Ba}^- \) and \( \text{NH}_4^- \)-exchangeable potassium showed the neutral barium chloride to be a suitable extractant for potassium.

Accurate direct-potentiometric determinations of the \( \text{NH}_4^- \)-exchangeable potassium were not feasible, even at pH 11.6. But, the \( \text{NH}_4^- \)-exchangeable potassium values obtained with the VKE and a modified standard additions
technique were highly correlated (r=0.987) and not significantly different (α=0.05) from those obtained by AAS. A single operator can perform about 100 analyses in a normal working day using either the direct or standard additions technique.
INTRODUCTION

When plants are grown on soils, they utilize varying amounts of the water-soluble, readily-exchangeable and slowly-releasable fractions of the soil potassium (K) [4]. In addition, the interrelationships between these forms of potassium and the structural potassium in minerals play a major role in the chemical properties and development of soils [12]. Thus, the role and fate of potassium in the soil continue to attract considerable attention. The availability of appropriate methods of determining the levels and dynamics of potassium under a variety of conditions is a fundamental requirement for this research. Usually, increments of potassium are separated from the soil and determined by atomic emission spectrometry (AES) or atomic absorption spectrometry (AAS). However, advances over the past 20 years in ion-selective electrode (ISE) technology have opened up new avenues for the characterization of potassium in soils. The advantages in using potassium ion-selective electrodes (K-ISEs) include (1) simple, nondestructive analysis, (2) potassium ion activity rather than concentration measurements, (3) automated analyses, (4) continuous monitoring capabilities, and (5) the possibility of in situ potassium determinations. Yet, despite these advantages, only rarely have K-ISEs been used in soil investigations.

The first commercially available K-ISEs were the cationic glass electrodes (CGEs) developed during the period from 1955 to 1965 and based on the glass compositions developed by Eisenman [6,7]. Mortland [18] was the first to use a CGE to measure the potassium in soils. He extracted the exchangeable potassium with 0.5 M magnesium acetate in a 1:10 soil-
extractant ratio, and measured the potassium in the suspension with the CGE and in the supernatant solution by AES. Although the two sets of exchangeable potassium values were highly correlated (r=0.90), the CGE yielded consistently and significantly higher values than did AES. The differences in the potassium values could be attributed to interferences from exchangeable Na⁺ and NH⁴⁺ in the suspensions. Likewise, CGEs have also been used to determine potassium ion activities in aqueous soil suspensions and pastes [14,15] and to determine the concentrations of soluble and Ba-exchangeable potassium in soil extracts [8], with similar results. Jacobson [13] showed that NH⁴⁺ interference could be reduced by using a high pH buffer to convert the NH₄⁺(aq) to NH₃(g), while Vytras [25] suggested using formaldehyde to complex NH⁴⁺, as hexamethylenetetramine, in alkaline solutions. Interferences resulting from varying levels of Na⁺ in the soil solutions, however, have not been resolved with the CGEs.

Fortunately, highly selective K-ISEs incorporating the ionophore valinomycin [10,21] have been developed and are commercially available. These valinomycin-based K-selective electrodes (VKEs) reportedly have selectivity ratios on the order of 10,000:1 for K⁺ over Na⁺, 1000:1 for K⁺ over H⁺ and 100:1 for K⁺ over NH⁴⁺ as compared to ratios of 10:1, 1:3 and 1:1, respectively, for the CGEs [1,3]. Yet, even though VKEs have been available for more than a decade, there have been few reports of their use in soil investigations [25]. Banin and Shaked [2] used a VKE to study potassium activity-concentration relationships in soil-water extracts, while Farrell [8] used a VKE to determine the concentration of soluble and Ba-exchangeable potassium in soil extracts. In the latter study, ammonium
interference was reduced by complexing the ammonium with formaldehyde in alkaline solutions; however, this procedure proved to be tedious and subject to interference from excess formaldehyde. More recently, a VKE has been used to determine potassium quantity-intensity relationships for several soils [20].

These studies, in addition to demonstrating the versatility of K-ISEs, suggest that further investigations into their general application are warranted. The fundamental requirements of electrochemical cells for potassium determinations as well as the performance of various K-ISEs and ways of minimizing ammonium interferences were investigated and the results reported elsewhere [9]. The objectives of this study were (1) to develop methods for the determination of Ba- and NH4-exchangeable potassium by ISE and (2) to compare the exchangeable potassium values obtained by ISE and standard flame methods for 30 Iowa soils.
EXPERIMENTAL

The soils used in this study included 15 surface and 15 subsurface samples selected to represent the range of exchangeable potassium normally encountered in Iowa soils. They were passed through a 2-mm sieve and air-dried.

Potassium Extractions

Exchangeable potassium was extracted using a modification of the method described by Scott and Welch [22]. Air-dried, 10 g soil samples were shaken with 50 ml neutral, 1.0 M ammonium acetate or 0.5 M barium chloride for 30 min, filtered and leached with an additional 25 ml of the extractant. The filtrates were then transferred to 100 ml volumetric flasks and brought to volume with additional extractant, transferred to polyethylene bottles, and stored in a refrigerator until analyzed.

Analytical Determinations of Potassium

Spectrometry

The amounts of ammonium acetate and barium chloride exchangeable potassium were determined using a Perkin-Elmer Model 560 atomic absorption spectrometer. The standard and sample solutions were prepared at a constant concentration of ammonium acetate (0.2 M) or barium chloride (0.1 M) and contained 1000 mg Na+ L⁻¹ as a radiation buffer.

Potentiometry

The ammonium acetate and barium chloride exchangeable potassium were determined using a Corning pH/Ion meter 135, an Orion 90-02 double-
junction sleeve-type reference electrode with a saturated lithium acetate salt bridge, and an Orion 93-19 K-selective electrode (OVKE). The barium chloride exchangeable potassium was also measured using a Beckman 39137 cationic glass electrode (BCGE). Aliquots of the soil extracts were diluted with deionized water (1:5 extract-water ratio), titrated to pH 11.6 with 3.0 M lithium hydroxide [9], and analyzed using the techniques described below.

**Direct potentiometry** The electrodes were immersed in the test solutions and cell e.m.f. values (E) were recorded when the rate of change was \( \leq 0.1 \text{ mV min}^{-1} \). All measurements were performed at 22±0.1°C in plastic beakers, with the test solutions mixed at constant speed. The electrodes were rinsed with 10 M potassium chloride and lightly blotted dry between measurements. The potassium ion concentrations were calculated from calibration curves obtained with standard solutions containing 0.25-10 mg K⁺ L⁻¹ (Figure 1). Alternatively, if the potassium ion concentration of the sample solutions was greater than or equal to the potassium ion concentration at the lower limit of linear response (LLLR in Figure 1), the Corning pH/Ion meter 135 could be programmed to display the results in concentration units directly.

**Standard additions** In general, the electrodes are immersed in a sample solution of known volume (\( V_x \)) and unknown potassium ion concentration (\( C_x \)) and the cell e.m.f. (\( E_x \)) is recorded; a known volume (\( V_a \)) of a concentrated potassium standard (\( C_a \)) is then added and the new cell e.m.f. (\( E_a \)) is recorded. The potassium ion concentration of the sample can then be calculated from the equation:
Figure 1. Calibration curves showing the response of the Orion K-selective electrode (VKE) in 0.2 M NH₄OAc and 0.1 M BaCl₂ solutions at a LiOH-adjusted pH of 11.6.
\[ C_x = \frac{V_a}{V + V_a} \cdot C_a - \frac{V_x}{10^{\Delta E/S} - \frac{V_x}{V + V_a}} \]

where \( S \) is the slope of the calibration curve (mV/10-fold change in potassium ion concentration). This equation is derived from the Nernst equation applied to the cell e.m.f. before \( (E_x^a) \) and after \( (E_a^*) \) the standard addition. Alternatively, \( C_x \) can be determined graphically by extrapolation of a plot of \( 10^{E/S} \) vs added potassium (mg L\(^{-1}\)), similar to the technique used in AES and AAS. The Corning pH/Ion meter 135 can be programmed, utilizing equation (1), to display the value of \( C_x \) directly. However, accurate potassium determinations can be made only if \( C_x \geq \text{LLLR} \). Since this may not always be the case, and since the best results are obtained when \( C_a \) is 2-3 times \( C_x \) [19], it was advantageous to "spike" the samples with a known amount of potassium prior to analysis and then triple this amount during the actual addition procedure. Specifically, our method involved spiking 10 ml aliquots of the ammonium acetate extracts with 1 ml of a 200 mg L\(^{-1}\) potassium standard, titrating to pH 11.6 with 3.0 M lithium hydroxide and diluting with deionized water to a volume \( (V_x) \) of 50 ml. The "standard addition," then, was 3 ml of the same potassium standard. The Corning pH/Ion meter 135 was programmed in the known (standard) additions mode (the slope having been calculated from a two-point calibration at 4 and 20 mg K\(^+\) L\(^{-1}\)) and the analyses were performed following the general procedure outlined above. The displayed values of \( C_x \) were then corrected for the potassium "spike" (i.e., 4 mg K\(^+\) L\(^{-1}\)) to
yield the original potassium ion concentration (C₀) of the diluted extracts (i.e., C₀ = Cₓ - 4 mg K⁺ L⁻¹).
RESULTS AND DISCUSSION

Barium Chloride Exchangeable Potassium

Most Iowa soils contain between 30 and 200 μg g\(^{-1}\) of exchangeable potassium with a median value of about 100 μg g\(^{-1}\) \[5\]. Thus, for a 1:10 soil-extractant ratio, the extract will contain between 3 and 20 mg K\(^+\) L\(^{-1}\). To accurately measure this potassium using an ISE, the NH\(_4\)\(^+\) concentration of the test solution should be less than five times the potassium concentration \[9\]. As this condition may be difficult to achieve when a 1.0 M ammonium acetate (∼18,000 mg NH\(_4\)\(^+\) L\(^{-1}\)) extracting solution is used, an alternative extractant was sought. Malcolm and Kennedy \[16\] and Farrell \[8\] have used barium chloride as the extractant in potassium exchange reactions when the extracted potassium was determined by ISE. However, it has been reported that barium salts extract less potassium from soils than ammonium acetate \[11,17\]. Thus, the effectiveness of barium chloride as an extractant for exchangeable potassium was evaluated by comparing the amounts of potassium extracted by neutral solutions of 1.0 M ammonium acetate and 0.5 M barium chloride (Figure 2). The two sets of potassium values obtained by AAS are highly correlated, but as indicated by the slope of the regression line the NH\(_4\)-exchangeable potassium values generally exceed the Ba-exchangeable potassium values. It is believed that the slightly lower potassium values obtained with the barium chloride extractions are due to potassium reversion upon rewetting of the air-dried soil samples. Nevertheless, Ba\(^{2+}\) is an efficient replacing cation and because of the high selectivity of the CGE and VKE for K\(^+\) over...
Figure 2. Relationship between the barium- and ammonium-exchangeable potassium determined by atomic absorption spectrometry (AAS).
Ba\(^{2+}\) it is an excellent alternative to NH\(^{4+}\) for the extraction of exchangeable potassium in these soils.

Direct potentiometric measurements of the exchangeable potassium in the barium chloride extracts were made with both the BCGE and the OVKE; and the potassium values thus obtained were compared to those obtained by AAS. The potassium values obtained with the BCGE, without any pH adjustment, are significantly greater than and poorly correlated with those obtained by AAS (Figure 3). Conversely, the potassium values obtained with the OVKE, in the same solutions, are highly correlated with and not significantly different from those obtained by AAS (Figure 4). The poor results obtained with the BCGE can be attributed to the presence of significant and variable amounts of interfering ions, most notably Na\(^+\), NH\(^{4+}\), and H\(^+\), in the extracts and the low selectivity of the electrode for potassium with respect to these ions. The OVKE, with its greater selectivity for potassium [9], is relatively unaffected by these interferents at the levels present. The slope and intercept of the regression line in Figure 4, however, indicate that some interference with the OVKE occurs at low potassium levels. (If the samples containing exchangeable potassium levels less than 50 \(\mu g \ g^{-1}\) are eliminated from the statistical analysis, the regression line becomes: \(\hat{y} = 0.982x + 3.6\), with \(r=0.987\) and \(F=0.23ns\).) Titrating the test solutions to pH 11.6 virtually eliminates all the interference from exchangeable NH\(^{4+}\) and H\(^+\); and the potassium values obtained with the OVKE are very highly correlated with and nearly identical to those obtained by AAS (Figure 5). Analysis of these pH-adjusted solutions with the BCGE was not feasible due to the response
Figure 3. Relationship between the barium-exchangeable potassium determined with the Beckman cationic glass electrode (CGE) and by atomic absorption spectrometry (AAS)
Figure 4. Relationship between the barium-exchangeable potassium determined with the Orion K-selective electrode (VKE) and by atomic absorption spectrometry (AAS)
Figure 5. Relationship between the barium-exchangeable potassium determined with the Orion K-selective electrode (VKE) and by atomic absorption spectrometry (AAS). The diluted extracts had a LiOH-adjusted pH of 11.6 for the VKE analysis.
of the glass electrode to the added lithium. However, in an earlier study where \( \text{NH}_4^+ \) and \( \text{H}^+ \) interferences were reduced with a formaldehyde-barium hydroxide treatment at pH 10 [8], the BCGE still yielded significantly higher potassium values (\( F=46^{**} \)) than AAS, presumably due to \( \text{Na}^+ \) interference.

The data presented in Figures 2-5 indicate that (1) barium chloride is an effective extractant for exchangeable potassium, (2) the presence of exchangeable \( \text{Na}^+ \), \( \text{NH}_4^+ \), and \( \text{H}^+ \) in the Ba-extracts prevents accurate potassium determinations by CGE, (3) exchangeable \( \text{NH}_4^+ \) can interfere with the determination of exchangeable potassium by VKE, particularly at low potassium levels, and (4) at pH 11.6, low-level \( \text{NH}_4^+ \) interferences are effectively negated and accurate VKE measurements of the potassium in Ba-extracts can be made.

**Ammonium Acetate Exchangeable Potassium**

The most common method of extracting the exchangeable potassium from soils involves replacement of the potassium ions on the exchange complex by ammonium ions (i.e., extraction with neutral, 1.0 M ammonium acetate). Thus, ISE determinations of potassium in ammonium acetate extracts are desirable. Clearly, however, before the potassium in these extracts can be measured by an ISE, the concentration of \( \text{NH}_4^+ \) in the test solutions must be greatly reduced. Based on the results of a companion study [9], aliquots of the ammonium acetate extracts were diluted with deionized water and titrated with 3.0 M lithium hydroxide to pH 11.6 to minimize the \( \text{NH}_4^+ \) interference. Furthermore, since the data obtained with the barium chloride extracts clearly demonstrate the superiority of the OVKE for
potassium determinations in soil extracts, the BCGE was not used in this phase of the investigation.

At a pH of 11.6, only about 0.4% of the NH₄⁺ in solution remain in the cationic form. However, since this percentage remains constant, the NH₄⁺ concentration after the pH adjustment depends on the initial concentration of NH₄⁺. Thus, the extract-water dilution ratio was investigated prior to analysis of the soil extracts. Calibration curves obtained with standard solutions representing 1:5 and 1:10 extract-water dilution ratios are presented in Figure 6. It was calculated that for a 1:5 extract-water dilution the test solutions would contain a median concentration of 2.2 mg K⁺ L⁻¹, which is about 22% greater than the LLLR (1.8 mg K⁺ L⁻¹), and that only eight of the soil extracts would contain potassium at concentrations less than the LLLR. Although at higher dilutions the effects of NH₄⁺ interference decrease, as evidenced by the downward shift in the LLLR (to 1.5 mg K⁺ L⁻¹), so does the median concentration of potassium (to 1.1 mg L⁻¹). And at a 1:10 dilution only six of the soil extracts contain potassium at concentrations greater than the LLLR. Further investigations revealed that there was no advantage in using dilutions less than 1:5. Therefore, potentiometric determinations of potassium in ammonium acetate extracts were made using the OVKE and 1:5 extract-water dilutions at pH 11.6.

Direct potentiometric measurements of the potassium in these diluted extracts yielded exchangeable potassium values that are highly correlated with but significantly greater than those obtained by AAS (Figure 7). These differences in the potassium concentration should not be due to
Figure 6. Calibration curves showing the response of the Orion K-selective electrode (VKE) in 1:5 (0.2 M NH$_4^+$) and 1:10 (0.1 M NH$_4^+$) NH$_4$OAc extractant-water dilutions.
Figure 7. Relationship between the ammonium-exchangeable potassium determined by direct potentiometry (with the VKE and pH 11.6) and by atomic absorption spectrometry (AAS)
interferences from soil contributed NH$_4^+$ because the NH$_4^+$ concentration of the standard solutions was 0.2 M. Moreover, the difference between the two sets of potassium values increases as the K$^+$ concentration increases. The reason for this effect is still unknown.

In atomic emission and absorption spectrometry, the technique of "standard additions" is commonly used to circumvent interference problems. With some reservations, this technique may also be used for potentiometric measurements [1,19,24]. Potassium measurements with the OVKE were made using the modified standard additions technique described previously, and the exchangeable potassium values thus obtained were compared with those obtained by AAS (Figure 8). The two sets of potassium values were highly correlated and not significantly different. However, the slope and intercept of the regression line indicate that ammonium interference still presents a problem at low potassium concentrations. (Eliminating those samples with exchangeable potassium values <90 µg g$^{-1}$ from the statistical analysis, the regression line becomes: $\hat{y} = 0.971x + 3.9$, with r=0.984 and F=0.09ns.)

The data presented on Figures 7 and 8 demonstrate that although the exchangeable potassium in NH$_4$-extracts cannot, as yet, be accurately measured using direct potentiometric methods, accurate measurements can be made using a modified standard additions technique.

Since expanded scale pH/mV meters are standard equipment in most laboratories these ISE methods can provide a simple, accurate and inexpensive alternative to flame analysis methods of determining
Figure 8. Relationship between the ammonium-exchangeable potassium determined by a standard additions method (with the VKE and pH 11.6) and by atomic absorption spectrometry (AAS)
exchangeable potassium. A single operator can perform upwards of 100 analyses in a single day.


SECTION III. CONSTRUCTION AND EVALUATION OF A POTASSIUM-SELECTIVE TUBE-MOUNTED MEMBRANE ELECTRODE
ABSTRACT

A simple procedure for the rapid construction of inexpensive potassium-selective electrodes with valinomycin-based PVC membranes is described. Potassium-selective membranes were formed on the end of Parafilm or Tygon covered glass tubes by dipping the tubes into a mixture of PVC, valinomycin, and dioctyl sebacate dissolved in tetrahydrofuran. Small internal Ag,AgCl reference electrodes were prepared with silver wire and placed inside the tubes with AgCl-saturated potassium chloride solution to complete the construction of the potassium-selective electrodes. This procedure yields tube-mounted membrane electrodes that perform as well as commercially available potassium-selective electrodes in terms of their response characteristics and practical applications with soil extracts. Moreover, it facilitates the evaluation of membranes with different compositions for making ion-selective electrodes.
INTRODUCTION

Potassium-selective electrodes incorporating the neutral carrier valinomycin in PVC membranes have become extremely popular during the past decade [4,7]. These electrodes, which can be constructed with either an internal reference solution [5,6] or a solid internal contact [10], have proved to be both reliable and versatile. Construction of these electrodes, however, can be quite cumbersome and, in some instances, may require specially designed membrane housings [5,10]. Furthermore, although potassium-selective PVC membrane electrodes are commercially available through several manufacturers [3,9], they are relatively expensive, as are the membrane replacements periodically required. Here, we report on a simple, rapid and inexpensive method of constructing potassium-selective tube-mounted membrane electrodes with valinomycin-based PVC membranes and Ag,AgCl internal reference elements.
EXPERIMENTAL

Electrodes

The membrane material for the potassium-selective electrodes consisted of a PVC-valinomycin-plasticizer mixture [5] prepared by dissolving 5 mg valinomycin (Sigma Chemical Co., U.S.A.) in 0.92 ml dioctyl sebacate (DOS) in a screw-cap centrifuge tube, adding 150 mg PVC and 2 ml tetrahydrofuran (THF) as solvent, and mixing thoroughly with a vortex mixer. Twenty or more electrodes can be prepared from this amount of material, which if refrigerated will keep for at least a year.

The Ag,AgCl internal reference electrodes were prepared by a modification of the procedure described by Bailey [1]. A 2.5-cm length of 20-gauge (B&S) silver wire was welded to a 20-cm length of 18-gauge (B.C.) copper wire, dipped into a solution of PVC (500 mg dissolved in 3-4 ml THF) several times, and air-dried. Approximately 1.5 cm of the PVC coatings was removed from the tip end of the silver wire, which was then dipped in concentrated ammonia solution for 30 s, rinsed with deionized water, dipped in 50% nitric acid until an even white color developed (~60 s), and rinsed again. By using a 500-KΩ, 10-turn, 3/4 W potentiometer to regulate the current from a 9-V battery, the silver wire was first made cathodic against a platinum anode in 0.1 M hydrochloric acid for 15-30 s at a current density that just produced bubbles at the silver cathode (~0.3 mA mm⁻²). The battery connections were then reversed, and the silver wire was made anodic at the same current density for 5-10 min. Properly prepared electrodes had a uniform purple-grey color and were stored in AgCl-saturated 10⁻³ M potassium chloride.
The tube-mounted membrane electrodes were constructed as follows. Membranes were formed on the ends of glass tubes (2 mm i.d.) by dipping the tubes in the PVC mixture and air-drying overnight. Because of the poor adhesion between glass and PVC and the nonavailability of rigid small-diameter PVC tubing, a narrow band (~5 mm) around the tip end of the glass tubes was wrapped with Parafilm or covered with Tygon tubing (3 mm i.d.) before they were dipped. The THF in the PVC mixture dissolved enough of the Parafilm or Tygon to glue the PVC to the glass covering and thereby achieve a good seal between the membrane and the tube. When the membranes had dried, the tubes were partly filled with AgCl-saturated $10^{-3}$ M potassium chloride in which the internal Ag,AgCl reference electrodes were then immersed, and the upper ends of the tubes were sealed with Parafilm. The potassium-selective electrodes thus prepared were conditioned in $10^{-5}$ M potassium chloride for 1-2 h and calibrated.

Orion 93-19 and Corning 476132 potassium-selective electrodes were similarly conditioned and calibrated. An Orion 90-02 double-junction sleeve-type reference electrode with a saturated lithium acetate salt bridge was used in all calibrations.

Apparatus and Experimental Techniques

Cell e.m.f. values ($E$) were measured with a Corning pH/Ion 135 meter and recorded when the rate of change was $\leq 0.1$ mV min$^{-1}$. All measurements were performed at 22±0.1°C in plastic beakers, with the test solutions mixed at constant speed. The potassium-selective electrodes were stored in $10^{-3}$ M potassium chloride when they were not to be used for periods of 2 or more days; otherwise, in $10^{-5}$ M potassium chloride. Calibration
measurements were carried out in sequence from dilute to more concentrated solutions, the electrodes being rinsed with $10^{-6}$ M potassium chloride and lightly blotted dry between measurements. Before each complete calibration sequence, the electrodes were soaked in $10^{-6}$ M potassium chloride for 15–20 min.
RESULTS AND DISCUSSION

Typical calibration curves for the potassium-selective tube-mounted membrane electrodes are shown in Figure 1. The cell potentials decreased at a rate of \( \approx 1.5 \text{ mV d}^{-1} \) during the first week, then at a rate of only \( \approx 0.2 \text{ mV d}^{-1} \) over the next month. Most of the rapid initial change was due to drift in the potential of the internal Ag,AgCl reference electrode as it equilibrated with the internal solution. This drift can be eliminated by equilibrating the Ag,AgCl electrode in AgCl-saturated \( 10^{-3} \) potassium chloride for 3-5 days before use. The later changes in the cell potentials are probably due to the effect of aging on the asymmetry potentials. Similar but smaller changes were observed with the Orion and Corning electrodes.

The response characteristics of the tube-mounted membrane electrodes (after 1 week of use) were very similar to those of the Orion and Corning electrodes (Table 1). The variations in cell constants \( (E^{\circ}) \) are presumably due to differences in the internal reference solutions of the electrodes and the asymmetry potentials of the membranes. The response times, i.e., the times needed for the \( \Delta E \) to become \( \leq 0.1 \text{ mV min}^{-1} \), for the electrodes were about the same: 3-5 min at low \( (<10^{-5} \text{ M}) \) potassium concentrations and 1-2 min at higher concentrations. The characteristics of all the electrodes were relatively unaffected by changes in pH from 5 to 11.

The tube-mounted membrane electrodes performed as well as or better than the commercial electrodes in practical determinations of potassium in soil extracts. A comparison of the results obtained with 0.5 M barium
Table 1. Experimentally determined response characteristics of various valinomycin-based K-selective electrodes

<table>
<thead>
<tr>
<th>Electrode type</th>
<th>E°&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Slope mV/mV/pK</th>
<th>LLL&lt;sup&gt;b&lt;/sup&gt;</th>
<th>LD&lt;sup&gt;c&lt;/sup&gt;</th>
<th>-log&lt;sup&gt;d&lt;/sup&gt;k&lt;sub&gt;KX&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tube-mounted A</td>
<td>270.0</td>
<td>57.6</td>
<td>8.9 0.35</td>
<td>1.1 0.043</td>
<td>1.95 4.38 4.92</td>
</tr>
<tr>
<td>Tube-mounted B</td>
<td>236.9</td>
<td>57.9</td>
<td>10.0 0.39</td>
<td>1.7 0.066</td>
<td>-- -- --</td>
</tr>
<tr>
<td>Tube-mounted C</td>
<td>226.4</td>
<td>58.4</td>
<td>6.1 0.24</td>
<td>0.86 0.034</td>
<td>1.96 4.93 5.78</td>
</tr>
<tr>
<td>Orion 93-19</td>
<td>81.2</td>
<td>58.6</td>
<td>6.8 0.27</td>
<td>0.89 0.035</td>
<td>1.94 4.11 4.90</td>
</tr>
<tr>
<td>Corning 476132</td>
<td>223.7</td>
<td>57.7</td>
<td>10.0 0.39</td>
<td>1.6 0.063</td>
<td>1.95 4.66 4.99</td>
</tr>
</tbody>
</table>

<sup>a</sup>Cell constant (consisting of the potential of the cell when a<sub>K</sub> = 1, the potentials of the internal and external reference electrodes, and the liquid junction and asymmetry potentials).

<sup>b</sup>Concentration of K<sup+</sup> at the lower limit of linear response.

<sup>c</sup>Limit of detection [2].

<sup>d</sup>The selectivity coefficients, k<sub>KX</sub>, were determined by the mixed solution method [1] with X=0.01 M NH<sub>4</sub><sup+</sup>, 0.1 M Na<sup+</sup>, or 0.1 M Ba<sup>2+</sup>.

chloride extracts of 10 soil samples and potassium determinations by the tube-mounted electrode C (TM-C), the Orion electrode and standard atomic absorption (AAS) procedures is given in Table 2.

The potassium-selective tube-mounted membrane electrode provides an excellent alternative to the more expensive commercial electrodes, especially in situations where the risk of damage to the membrane is high. Since the tube holding the membrane is quite small and can be even smaller, these electrodes are well-suited for determinations of potassium in small samples. Furthermore, many of these electrodes can be prepared at one time and the membranes can be easily removed and replaced.
Figure 1. Calibration results obtained with K-selective tube-mounted membrane electrode A; 1 day, 1 week, and 5 weeks after it was constructed.
Table 2. Comparison of the results obtained with K-selective electrode and atomic absorption determinations of BaCl₂-extracted soil K

<table>
<thead>
<tr>
<th>Method of K analysis</th>
<th>Soil K extracted (^a) (µg g(^{-1}))</th>
<th>No. of reps</th>
<th>CV (%)</th>
<th>(R^2)</th>
<th>AAS</th>
<th>Orion</th>
<th>TM-C</th>
</tr>
</thead>
<tbody>
<tr>
<td>AAS</td>
<td>109</td>
<td>3</td>
<td>2.65</td>
<td>1</td>
<td>0.962</td>
<td>0.994</td>
<td></td>
</tr>
<tr>
<td>Orion electrode</td>
<td>111</td>
<td>3</td>
<td>1.02</td>
<td>—</td>
<td>1</td>
<td>0.987</td>
<td></td>
</tr>
<tr>
<td>TM-C electrode</td>
<td>106</td>
<td>3</td>
<td>0.54</td>
<td>—</td>
<td>—</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)Mean of 10 soil samples.

This procedure for the construction of tube-mounted membrane electrodes was used to evaluate a variety of membranes with different compositions. Modifications in the K-selective membrane were carried out by changing the plasticizer, ionophore, and matrix to improve the selectivity and adaptability of the K-ISE.

Although only a secondary electrode component, the plasticizer may influence the properties of the membrane [8]. Consequently, various plasticizer types were evaluated to determine whether or not the selectivity of a given ionophore for K\(^+\) over NH\(_4^+\) could be enhanced. The plasticizers involved were dioctyl sebacate (DOS), dioctyl adipate (DOA), and dibutyl phthalate (DBP). It was found that changing the plasticizer had no significant effect on the selectivity of the electrodes (Table 3). However, when the ionophore was valinomycin, the plasticizers significantly affected the other electrode response characteristics. And when the ionophore dibenzo-18-crown-6 (DB-18-C-6) was used, these effects were markedly reduced. (It should be noted, however, that DB-18-C-6 was not
Table 3. Experimentally determined response characteristics of various tube-mounted membrane K-ISEs

<table>
<thead>
<tr>
<th>Ionophore</th>
<th>Matrix</th>
<th>Plasticizer</th>
<th>Slope (mV/pK)</th>
<th>LLLR</th>
<th>LD</th>
<th>log Pot</th>
<th>Pot KNH₄⁻</th>
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<tr>
<td>Valinomycin</td>
<td>PVC</td>
<td>DOS</td>
<td>59.1</td>
<td>0.56</td>
<td>0.083</td>
<td>1.96</td>
<td></td>
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<tr>
<td></td>
<td>DOA</td>
<td>57.8</td>
<td>1.4</td>
<td>0.28</td>
<td>1.95</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>DBP</td>
<td>54.6</td>
<td>2.7</td>
<td>0.47</td>
<td>1.93</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SR</td>
<td>-d</td>
<td>59.0</td>
<td>0.64</td>
<td>0.084</td>
<td>2.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DB-18-C-6</td>
<td>PVC</td>
<td>DOS</td>
<td>59.2</td>
<td>0.56</td>
<td>0.12</td>
<td>2.02</td>
<td></td>
</tr>
<tr>
<td></td>
<td>DBP</td>
<td>59.4</td>
<td>0.81</td>
<td>0.23</td>
<td>1.98</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LSD ( = 0.05)</td>
<td></td>
<td>0.3</td>
<td>0.24</td>
<td>0.10</td>
<td>0.13</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a Concentration of K⁺ at the lower limit of linear response.
b Limit of detection [2].
c The selectivity coefficients, Pot X⁻, were determined by the mixed solution method [1] with X=0.01 M NH₄⁺.
d No plasticizer necessary.

Based on these results, it was concluded that (1) regardless of the ionophore, optimum response of the PVC membrane electrodes was attained using the plasticizer DOS and (2) DB-18-C-6 was no better than valinomycin.

Modification of the membrane matrix was accomplished by substituting a silicone rubber (SR) and its associated cross-linking agent for the PVC and plasticizer components. Valinomycin-based tube-mounted SR membrane electrodes were constructed and evaluated in both aqueous and partially-aqueous KCl solutions. In aqueous potassium chloride systems, these electrodes were found to perform as well as the PVC membrane electrodes (Table 3). In addition, the SR membrane electrodes have demonstrated a
greater tolerance to partially-aqueous solutions. Figure 2 shows the calibration results obtained with a valinomycin-based PVC membrane electrode in aqueous potassium chloride and potassium chloride-40% acetone systems, while the results obtained with a valinomycin-based SR membrane electrode are shown in Figure 3. Although the results obtained with the SR membrane electrode are promising, several problems still remain; in particular, the electrodes have greatly reduced life-spans after exposure to the acetone systems.
Figure 2. Calibration results obtained with a valinomycin-based PVC membrane electrode, versus a Na-selective glass electrode (ISA = 0.1 M LiCl), in a sequence of KCl, KCl-acetone and KCl solutions.
Figure 3. Calibration results obtained with a valinomycin-based SR membrane electrode, versus a Na-selective glass electrode (ISA = 0.1 M LiCl), in a sequence of KCl, KCl-acetone and KCl solutions.
LITERATURE CITED


GENERAL CONCLUSIONS AND DISCUSSION

Although it was evident from the review of the current information about K-ISEs that potentiometric methods of studying potassium in soils and minerals were already available, they appeared to be limited to special conditions. Thus, this study was initiated as a part of a larger project on the electrochemical characterization of the forms, reactions, and relevance of potassium in soils and minerals. The results presented in the three sections of this dissertation have contributed a great deal of new information about the basic requirements of electrochemical cells for potassium determinations, the applicability of K-ISEs to soil extracts, and the feasibility of modifying K-ISEs to meet the unique requirements of soil and mineral systems. The first section dealt with the selection of a suitable reference electrode and procedures to minimize interferences. The second section dealt with an evaluation of K-ISE methods of determining exchangeable potassium in soil extracts. The third section dealt with the procedures that were devised to prepare and test different K-ISEs.

Section I concluded that although the use of K-ISEs in cells without transference requires a special pH/Ion meter if the reference electrode has a high impedance, they can be used for specific situations if the ion contributing to the potential of the reference half-cell can be kept constant, K impurities in the added salts are very low, and the response of each ISE is dominated by only one ion in the solution. In particular, a cell that consisted of a glass pH electrode, a VKE and a solution adjusted for ionic strength and pH by LiCl and LiOH-DEA, respectively, was
well-suited for K determinations when NH$_4^+$ interferences were negligible. When the NH$_4^+$ levels were not negligible, and particularly when they were not constant, a cell with transference was preferred. A sleeve-type double-junction reference electrode assembly with a saturated lithium acetate salt bridge provided the best results under all test conditions. Valinomycin-based K-ISEs circumvented the problems of interference from all the ions involved in soil potassium determinations except NH$_4^+$. Difficulties due to NH$_4^+$ could, however, be reduced by as much as 98\% by titrating the NH$_4^+$-solutions to pH 11.6-11.8 with lithium hydroxide.

In Section II, procedures using K-ISEs for the determination of Ba- and NH$_4^+$-exchangeable potassium in soils were described. The exchangeable potassium in 30 soil samples was extracted with neutral 0.5 M barium chloride and 1.0 M ammonium acetate and determined by AAS to establish the potassium levels sought with the K-ISEs. It was concluded that the best results were obtained using the VKE and a 1:5 extractant-water ratio titrated to pH 11.6 with lithium hydroxide. Accurate determinations of the Ba-extractable potassium were possible using direct potentiometric methods, while a modified standard additions method gave the best results for the NH$_4^+$-extractable potassium.

In Section III, a procedure for the rapid construction of inexpensive tube-mounted K-ISEs was described. This procedure yielded small K-ISEs that performed as well as the commercially available VKEs in terms of their response characteristics and practical applications with soil extracts. This procedure was used to evaluate membranes with different compositions for K-ISE applications in acetone-water systems.
The enormous potential of using K-ISEs in soil and mineral systems has only begun to be explored. At present, the concentration of K in the solution phase of soils can only be estimated because the available methods of displacing the solution, making water-soluble extracts, etc., change the potassium level. Micro K-ISEs should make the in situ determination of this potassium possible and ultimately show the relevance of this form of potassium. Also, instead of having to extract the various forms of potassium from different soil samples, a sequential determination of dissolved, exchangeable, and slowly releasable potassium in the same soil sample may be achieved with K-ISEs. From the literature on mica weathering it is clear that the exchangeability of interlayer potassium and in turn the selectivity of the mineral for potassium can be the dominant factor and that the rates and amounts of potassium exchange provide an excellent means of evaluating the role of other factors. The nondestructive and monitoring capabilities of K-ISEs will make it possible to obtain quantitative information on these aspects of an ongoing process.
ADDITIONAL LITERATURE CITED


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