Application of Ammonium Sensor for Environment Analysis

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Abstract - The need to analyze some chemical species in complex systems has brought a rapid advance in new analytical tools. Ammonium sensor for determination of ammonia in fertilizer samples is described in such context. It is based on a polyimide (PI) matrix selective device and it is compared with an ion-selective electrode (ISE) with polyvinyl chloride (PVC) membrane. Attempts to obtain also a workable ammonium selective membrane using polyetherimide (PEI) were unsuccessful due to poor solubility of the electroactive component. The polyimide based device shows good results for the ammonium content of the complex fertilizer samples when compared with those ones obtained with PVC based ISE. The sensor shows a slope of 55.13 mV.dec^{-1} and a good selectivity against potassium.

Keywords: ammonium sensor, complex fertilizer, environmental analysis, polyimide, selective membrane

I. INTRODUCTION

In the context of a strict framework of the environmental legislation, there is a great interest for continuous monitoring of the environment quality [1]. The high demand for complete and real time data regarding a variety of parameters is actually more important than ever in the complex and complete ecosystems. In such conditions, the need for new sensors able of quick and reliable answer is growing steadily. The most efficient fertilizers used are the complex ones, known as "NPK" fertilizers. These contain the major plant nutrients, "NPK" being the notation used for total nitrogen, i.e. ammonium and nitrate concentration together, P_2O_5 and K_2O. In simple terms, nitrogen compounds are used for leaf production, phosphates for root production and potassium compounds for flowering [2].

Conventionally, in industry, the composition of fertilizers is established by spectrophotometric method, chromatographic method, or through statistical evaluation method [3, 4].

But, when needed a rapid analysis on field, the ISE is the most convenient solution [5]. There is an increasing need for complete and real time data on various parameters monitoring the chemically hazardous materials for environment [6].

The overexploitation and non-rational use of fertilizers resulted in a deterioration of both the water and the soil [3]. According to the framework of various specific legislation provisions [1] there is an important demand for improving the quality control systems in order to maintain a suitable environment quality.

Much more, if we would extend the investigation area from the environmental issues to the clinical ones, it would clearly come out the advantages of the electrochemical methods [7]. For instance, the levels of urea and creatinine in blood are important diagnostic indicators of renal, thyroid, and muscle function. Some of the most appealing electrochemical techniques regarding sensitivity and specificity relay on the use of ion – selective membranes. Significant effort has been expended in developing reliable sensors for the detection of these analytes. At the present time, urea and creatinine levels are measured indirectly following enzyme-catalyzed hydrolysis to produce ammonium ions.

Typically, measurement of ammonium ion concentrations is achieved by carrier based ion selective electrodes (ISEs) containing the natural antibiotic nonactin as an ionophore [5]. In ISEs, a polymeric membrane lies between the aqueous sample containing the ion and an internal electrolyte solution. The membrane is doped with a selective ion carrier (nonactin in the case of ammonium) and a lipophilic salt that acts as an ion exchanger. The potential that develops at the membrane/sample interface is proportional to the activity (concentration) of ammonium ions in the aqueous sample. The two key properties of any ion sensor are sensitivity to the desired ion in the required concentration range and selectivity for one specific ion over all other interfering ions, properties that are primarily imparted by the ionophore.

Sensing of chemical parameters using potentiometric techniques is still an area for further development. While an important variaty of sensing techniques has been successfully tested during last decades only very few reached the market.

Lately, it is a great interest for advanced miniaturization of the ISEs due to the continuously reduced sample volume which has to be analyzed. The commonly used polymeric membranes based on PVC proved not to be entirely compatible with the technology of the sensors micro fabrication. For this reason, much effort has focused on the

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development of new selective membranes, particularly based on matrix with increased affinity for the specific metallic substrate (silicon) to improve the life time and the accuracy of the sensors [5, 7, 8].

The devlopment of ammonium selective device for environmental monitoring is discussed. Nonactine was used as ammonium ionophore (Figure 1). This electroactive component has a rigid framework with a cavity appropriately sized for ammonium ion (ionic radius 1.43 Å) necessary to impart high selectivity over interfering cations of other sizes.

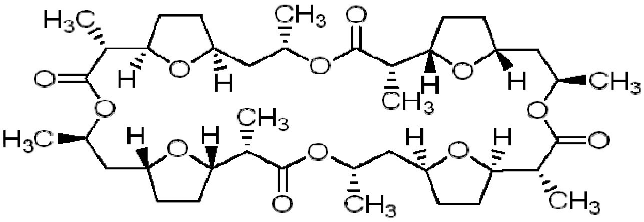


Figure 1. Nonactin

If the substrate is too flexible, it can change conformations to allow coordination with larger and smaller cations besides the desired ion. The ammonium ionophore should exhibit a spatial distribution of lone-pair electrons for effective hydrogen bonding with the tetrahedral ammonium ion. Interfering potassium ions are of similar size (1.33 Å) to ammonium ions, but have spherical symmetry and therefore prefer ionic bonds with coordination numbers of six or higher. For this reason, the coordination geometry is responsible for imparting selectivity for ammonium over potassium ions. Lastly, the ionophore should be highly lipophilic in order to be compatible with the non-polar membrane environment of ion selective electrodes [9] and to prevent extraction of the ionophore from the sensor during testing.

In this paper, we present ammonium selective devices based on preimidized polyimide (Aldrich) and polyetherimide (SABIC) as alternative polymeric matrix to PVC. Results obtained in different fertilizer analysis are presented sustaining the ammonium polyimide based sensor for environmental sensing.

II. EXPERIMENTAL

There were used PVC based selective membranes in order to use them as reference for our determinations. Ammonium – responsive PVC devices were obtained by casting ammonium – doped films from tetrahydrofuran (THF) solution over a PTFE support.

The following chemicals were used for preparing the PVC selective solutions: PVC high molecular weight - Breon, nonactin - Fluka, o-nitro phenyl octyl ether (o-NOPE) – Fluka, potassium tetra phenyl borate – Fluka, tetrahydrofuran (THF) – Fluka.

As the previous works proved that the purity of THF used as PVC solvent affected the sensor response-time and detection limit, then freshly double-distilled THF was used exclusively [10]. The membranes obtained were flexible, trasnparent and mecanically resistant (Figure 2).

The ammonium responsive devices based on polyimide (PI) used as polymeric matrix a 25% solution of polyimide in dimethyl formamide (DMF). Such solutions were prepared by dissolving commercially available pre-imidized polyimide (Aldrich) in anhydrous dimethyl formamide (DMF) at 110^{0}C under continuous stirring [11].

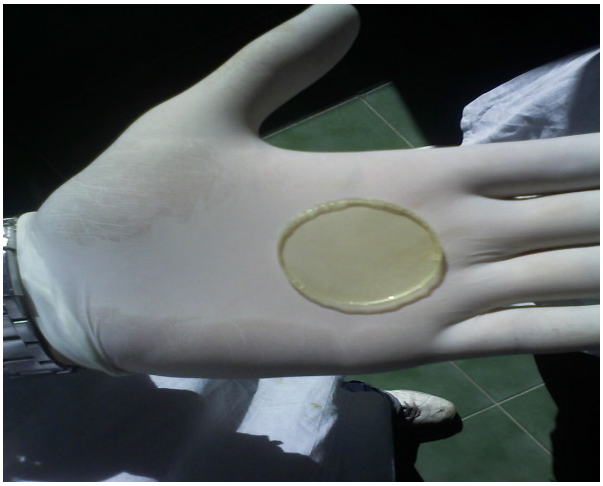


Figura 2. The PVC based membrane.

As plasticizer it has been used diethylene glycol dibenzoate (DGD) (Aldrich) [12]. The selective membrane had the composition as: nonactin (Fluka) – 0.7 %, polymer – 31%, plasticizer – 67%, potassium tetrakis 4-chloro phenyl borate (Fluka) as lipophilic salt – 0.3% [13]. All the percentages were by weight. Similarly, it has been obtained the polyetherimide (PEI) membrane. This polymer is an amorphous, amber-to-transparent with the glass transition temperature of 216 °C, as compared to 398^{0}C of PI [11].

After leaving the selective membranes for 24 h in desiccator for drying, the ISEs were obtained by mounting the cut ammonium membranes into a Philips electrode body. The membranes were conditioned over 24h with 10^{-2}mol.L^{-1} ammonium chloride internal solution and the membrane immersed in 10^{-2} mol.L^{-1} ammonium chloride. The calibration solutions were made using NH_4Cl (Fluka) in distilled water.

The devices were appraised using a series of calibration solutions of ammonium chloride (Analar grade), ranging between 10^{-1} mol.L^{-1} and 10^{-6} mol.L^{-1}. All appraisals were carried out at constant temperature, 25^{0}C.

The obtained devices were calibrated with correspondent calibration solutions as mentioned above. A double junction calomel reference electrode (Russell) was used in the performed studies. The measurements were done by help of a Cyberscan PCD 6500 from Eutech Instruments. The preliminary dip tests were carried out in order to ensure that sufficient conditioning time has been given to newly prepared electrodes, and as a mean of discarding faulty electrodes (not workable selective membranes). Electrodes were calibrated immediately prior to each analysis; this is important as a variation in the standard potential is often observed due to ageing of the system, although the Nernst slope is not affected.

The ammonium ISEs obtained with different polymeric inert matrix was used to analyse various sample of fertilizers provided by local manufacturer (Azomureş). The composition of these fertilizer samples are presented in Table 1.

Samples 1 to 3 were analysed as supplied, at dilute concentrations, 0.5 g.L^{-1} to 2.0 g.L^{-1} and were untreated. To a sample of 10 g.L^{-1} from fertilizers no.4 to no.6 it was added an ionic strength adjustment reagent (ISA), 2 mol.L^{-1} sodium sulphate in a 1: 50 v/v ratio, and these samples were analyzed.

Table 1. The composition of fertilizer samples (Azomureş)

Sample number	NPK Ratio	Sample concentration (g.L^{-1})	[NH$_4$] mol.L^{-1}
1	**15:15:21**	**1.0**	**4.240 x 10^{-3}**
2	**25:5:5**	**2.0**	**2.166 x 10^{-3}**
3	**10:25:15**	**0.5**	**1.581 x 10^{-3}**
4	**20:10:10**	**10.0**	**2.20* x 10^{-3}**
5	**15:15:15**	**10.0**	**1.50* x 10^{-3}**
6	**9:24:24**	**10.0**	**2.10* x 10^{-3}**

** values supplied by manufacturer*

None of the samples was filtered prior to analysis, t signifying that the samples under test were in suspension. This could give serious pH errors which in turn could affect speciation. Therefore, the fertilizers were filtered using medium glass sinter (no. 2). The pH of all the fertilizer samples, filtered and unfiltered was determined using a pre-calibrated glass electrode. The effect of the ionic strength adjustor on pH was also measured in both filtered and unfiltered samples of fertilizers 4 to 6.

As potassium is present in fertilizers as a phosphate-based compound, the electrochemical responses of the made ISEs were observed as the concentration of phosphate was increased.

Selectivity studies, using the mixed solution method and the constant volume dilution (CVD) method, were carried out to determine $k_{NH4+,K+}$ using 10^{-1} mol.L^{-1} ammonium chloride and 10^{-2} mol.L^{-1} potassium chloride.

III. RESULTS AND DISCUSSIONS

After 24 h it occurred the separation of the ionophore from the polyether imide membrane (PEI).

Our attempts to obtain a workable ammonium selective membrane using PEI were unsuccessful due to poor solubility of the ionophore within polymeric matrix as could be observed in Figure 3.

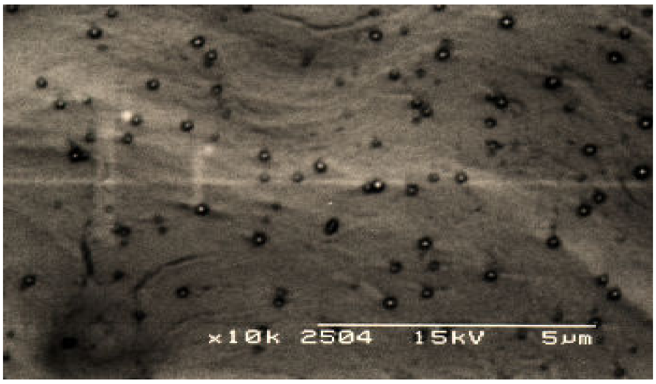


Figure 3. Morphology PEI membrane: polyether imide / dimethyl formamide/diethylene glycol dibenzoate/nonactine

The PVC based ammonium-ISE was calibrated using ammonium chloride solutions. A solution of 10^{-1} mol.dm^{-3} ammonium chloride was diluted using the constant dilution method. A Nernst response of 59.51 mV.dec^{-1} was calibrated for this ISE. It was noticed that the performance of electrodes deteriorated in time. Eventually, neither the PVC based ISE nor the polyimide based ISE responded to ammonium ions. Several attempts were made to reinstate the ISE's response by soaking the membranes in progressively more concentrated (up to 1.0 mol.L^{-1}) solutions of ammonium chloride, for extended periods of time (12 h to several days).

It was suspected that potassium ion, present in similar quantities to ammonium ion in the sample (Table 2) and of similar ionic radius was responsible for this behaviour.

Table 2. Concentrations of potassium ion present in the fertilizers samples.

No.	NPK Ratio	Expected [K$^+$], g.L^{-1}	Experimental [K$^+$], mol.L^{-1}
4	**20:10:10**	**0.9* x 10^{-3}**	**1.00^ x 10^{-3}**
5	**15:15:15**	**1.4* x 10^{-3}**	**86.60^ x 10^{-3}**
6	**9:24:24**	**4.0* x 10^{-3}**	**57.60^ x 10^{-3}**

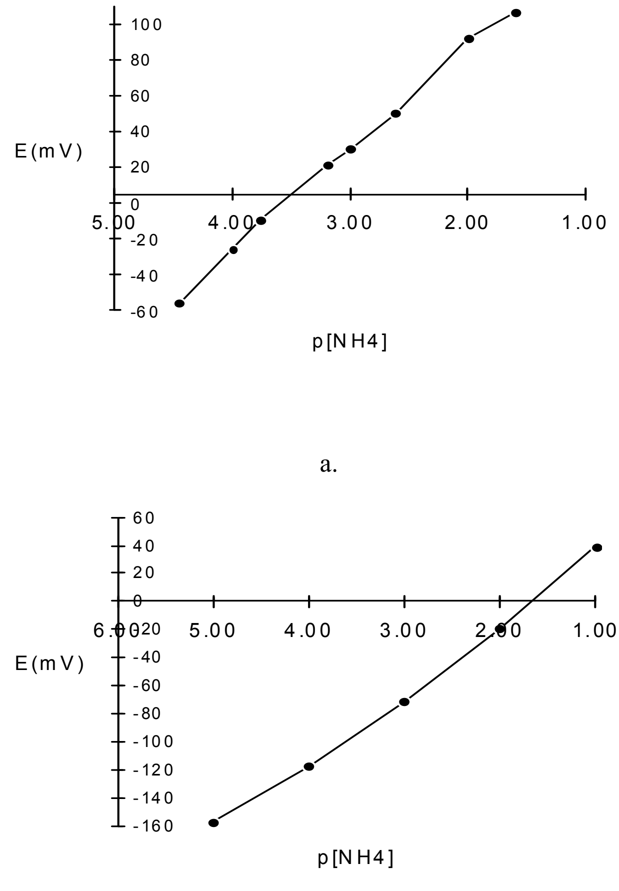
** values supplied by manufacturer*

^values determined using PVC based potassium ISE

Several new membranes and ISEs were prepared in order to reproduce the observed effect in a controlled experiment using standards of known concentrations of potassium ion.

Dip tests were carried out. Concentration of samples were all determined graphically from calibrations curves obtained for PVC based ISE and the PI based ISE, which are shown in figure 4 (a and b).

Measurements determined using the constant volume dilution method [14] presented in table 3 are compared with the expected (calculated) values.



a.

b.

Figure 4. Calibration curve for ammonium selective electrode; a. PVC based selective membrane; b. PI based selective membrane.

The data presented in table 3 show that the ammonium concentration values obtained using the constant volume dilution method (CVD) were about 10 times greater than those values determined using the dip test and the manufacturer's value.

Such results substantiated previous findings that the dead space in the dilution cell gives rise to erroneous concentration values of samples, due to inefficient mixing of sample and diluting solution, so that solutions appear to have higher concentrations then is actually the case.

Table 3. Ammonium analysis of fertilizers (1-3) with PVC based ISE.

	$[NH_4^+]$ / mol.L^{-1} x 10^3		
No.	**CVD**	**Dip method**	**Expected (Calculated)**
1	28.8	4.22	4.246
2	22.9	2.51	2.166
3	22.4	3.09	3.164

The ammonium concentrations of the samples 1 to 3 as determined by dip method, with the PVC and PI based ISE are shown in the table 4.

Table 4. Comparative analysis carried out on fertilizers 1-3.

	$[NH_4^+]$ /mol.L^{-1} x 10^3		
Sample No.	**PVC based ISE**	**PI based ISE**	**Expected (Calculated)**
1	4.22	3.69	4.246
2	2.51	2.66	2.166
3	3.09	3.47	3.164

It can be seen that the values obtained were closed to the calculated value for fertilizers from 1st batch. The ammonium concentrations determined for samples 4 to 6 did not agree well with the values supplied by the manufacturer, but were in general ten times greater than expected values, as shown in table 5.

Table 5. Comparatice analysis carried out on fertilizers 4-6.

	$[NH_4^+]$ / mol / mol.dm^{-3} x 10^3		
Sample no.	**PVC based ISE**	**PI based ISE**	**Expected (Calculated)**
4	10.61	13.50	2.20*
5	15.92	13.60	1.50*
6	25.48	27.70	2.10*

** values supplied by manufacturer*

The large discrepancy for these analyses as compared with the similar results obtained previously for fertilizers 1 to 3 could be considered suspect. It is for this reason that the effect of filtering and ionic strength adjustor (ISA) was investigated.

As the second batch of samples was more concentrated, 10 g.L^{-1} as opposed to 1.0 g.L^{-1} of the 1st batch of fertilizers, there was a higher degree of suspended matter. It was also noted that no potassium ions were detected in fertilizers 1 to 3, but significant amounts were present in samples 4 to 6.

Brezinski [15] emphasised the restrictions imposed on ISEs in colloidal samples with respect to colloidal charges and inhomogenity of the sample. The pH difference between colloidal sediments and the supernatant liquid was assigned the term "suspension effect" by Pallman and Weigner [16]. They attributed this pH variation to the absorption of hydrogen ions by dispersed phase.

However, the position of the reference electrode affected the magnitude of suspension effect. This effect has to be taken into account as well when assigning the unequal partition of hydrogen ions between the supernatant liquid and the charged colloid particles as a result of a phase boundary potential that is Donnan potential at the solid supernatant interface [17]. In general, the pH of a suspension appears lower than anticipated if a suspension effect is present.

No significant pH differences were observed during our experiments between filtered and unfiltered samples. In the most concentrated sampled, as 4 to 6, a pH difference of only -0.03, 0.02 and +0. 09 in pH units were observed between the filtered and unfiltered samples. These results could be followed in table 6.

Table 6. pH effect of filtering fertilizer samples.

Sample no.	Unfiltered pH	Filtered pH	Δ pH
1	6.56	6.57	+ 0.01
2	6.56	6.55	- 0.01
3	6.33	6.32	- 0.01
4	6.51	6.60	+ 0.09
5	6.61	6.63	+ 0.02
6	5.84	5.81	- 0.03

It was also shown that the presence of ISA did not influence the pH readings in filtered or unfiltered samples (table 7). In neither of the pH tests was observed a trend. If any significance could be attached to the small ΔpH changes observed, one would expect all pH changes to be negative (between filtered and unfiltered samples), this is evidently not the case. Nor was the direction of pH change consistent in experiments concerning ISA.

Therefore, it can be concluded that no suspension effect was observed during this work and the changes in pH observed between experiments was not due to suspended matter.

The discrepancy between the manufacturers' results and those using electrochemical methods may have arisen due to inherent properties of each technique. The ISEs detect only ionised ammonium and report activity of primary ion, whereas spectrophotometric methods report total concentration of species of interest. This further complicates the issue, as one would expect the manufacturers' results to be greater than those obtained by electrochemical method.

Table 7. pH effect on addition of Ionic Strength Adjuster (ISA).

No.	Unfiltered samples pH		Δ pH	Filtered pH		Δ pH
	With ISA	no ISA		With ISA	no ISA	
4	0.65	6.51	- 0.06	6.51	0.60	+0.09
5	0.59	6.61	0.02	6.62	0.63	+0.01
6	5.74	5.84	+0.07	5.76	5.81	+0.05

The ammonium calibration solutions used were ammonium chloride (10^{-1} to 10^{-5} mol.L^{-1}); however, the fertilizer samples are extremely complex, containing phosphates, nitrates and other chemical species. The ionic strength of the fertilizer samples is, therefore, much greater than that predicted by ammonium concentration alone.

The same standards were used for ammonium determinations of fertilizers 1 to 3 and fertilizers 4 to 6, of 0.5 – 2.0 g.L^{-1} and 10 g.L^{-1} sample concentration, respectively. There was, therefore, a considerable difference in the ionic strength between the two batches of fertilizers, and in consequence large differences in the liquid junction potentials experienced by each system. A twenty fold difference in concentration between samples 1 to 3 an 4 to 6 could give rise to a difference in the liquid junction potential, E_{LJ}, of about 10 mV, which relates to a difference in the concentration of 1,67x10^{-2} mol.L^{-1} for a 10^{-1}mol.L^{-1} solution. This could explain, in part, why experimental values obtained for the ammonium ion concentration of samples 1 to 3 were considerably nearer those values obtained for samples 4 to 6.

As consequence, it is important that the chemical composition of the standards should match as closely as possible to that of the samples [18].

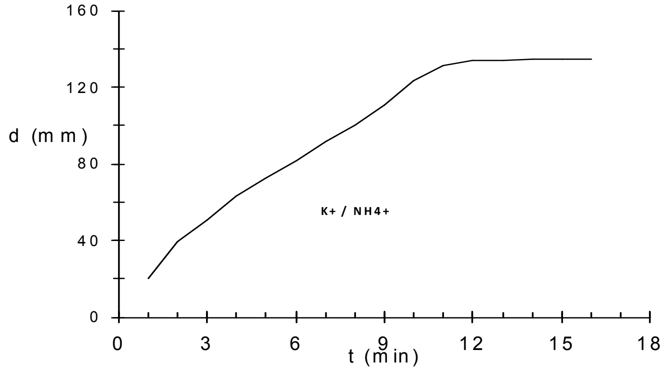


Figure 5. Determination of the selectivity $k_{NH4+, K+}$ for PI based ammonium ISE; mixed solution method. (chart recording speed = 200 mm.h^{-1}, full scale deflection = 200 mV, flow rate = 4.97 ml.min^{-1}, volume of the dilution vessel = 32.40 ml).

A variation of the matrix between the calibrants and the samples can lead to a considerable liquid junction error [17]. As a result of these inconsistencies, tests would also have to be carried out to ascertain the effect of potassium and phosphate ions.

The results of mixed solution selectivity tests, shown in figure 5 using the PI based ISE were reproducible and gave an average $k_{NH4+, K+}$ of 7.4 x 10^{-2} (figure 6). According to the extended Nernst equation a sensor is selective if the selectivity coefficients for the interfering ions are small. Practically the selectivity coefficient should be smaller than 10^{-3}, which means that the excess of the interfering ion has to be 1000 times more concentrated than the measuring ion to be detected as good as this.

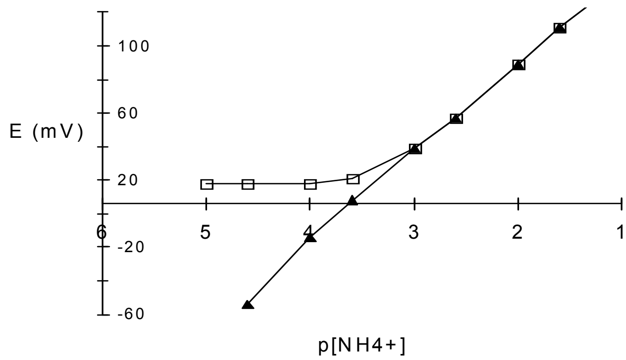


Figure 6. Selectivity study of $k_{NH4+,\ K+}$ using PI based ammonium ISE by constant volume dilution method.

The concentration of ammonium ions is very similar to the potassium ions concentration; one would consequently expect some interference. This argument is further substantiated when one realises that samples 1 to 3, which contained a detectable potassium ion concentration gave values close to the manufacturer's specifications.

The effect of potassium ion interference on the values of ammonium ions is presented in table 8.

Table 8. Effect of potassium ions on ammonium ion signal.

Sample no.	Manufacturer's values x 10^{-1} (mol.L^{-1})			Experimental values	
	$[NH_4^+]$	$[K^+]$	$[K^+]+[NH_4^+]$*	$[NH_4^+]$ PVC -ISE	$[NH_4^+]$ PI- ISE
4	0.2	0.9	1.0628	10.61	3.5
5	0.5	1.4	0.5110	15.92	3.6
6	2.1	4.0	2.1554	25.48	22.7

All concentrations in mol.L^{-1}.

**Using $k_{NH4+,\ K+}$ = 7.4 x 10^{-2} , this value represents the combined concentration of the primary ammonium ion and interfering potassium ion.*

As selectivity coefficient is dependent on the method of its determination and decreases with increasing concentrations of the interfering ion, the found results show an improvement in the selectivity against potassium.

The combined concentration of ammonium and interfering potassium ions does predict a slightly larger signal will be observed by the ammonium selective ISE, but this still does not fully explain the greater than tenfold difference between observed and expected ammonium concentration values for all of 10 g.L^{-1} samples. It is considered that the effect of phosphate on ammonium ion ISEs has to be investigated further.

The Nernstian response of the electrodes as the study continued from 58.73 mV.dec^{-1} and 55.13 mV.dec^{-1}, respectively to no ammonium response. Despite soaking in solutions of ammonium chloride of 1.0 mol.L^{-1} for several days, the ammonium response could not be restored. The previously determined selectivity coefficient of the PI based ISE showed that it was susceptible to potassium ion interference.

It was not possible to reproduce this "poisoning" effect with any of several newly prepared ISEs. An electrode dipping overnight in a 1.0 mol.L^{-1} potassium chloride solution, showed a Nernst response to ammonium after being in 10^{-2} mol.L^{-1} ammonium chloride for 2 h. Similarly, an electrode soaked for 60 h in a solution of 10^{-1} mol.L^{-1} potassium chloride and 10^{-4} mol.L^{-1} ammonium chloride showed a slight decline in performance, from 52.5 mV.dec^{-1} to 48.4 mV.dec^{-1}, but the Nernstian response was improved after being in 10^{-1} mol.L^{-1} ammonium chloride overnight.

In order to determine how effectively potassium ions remained in the selective membrane, sequential aliquots of a 10^{-1} mol.L^{-1} potassium chloride / 10^{-4} mol.L^{-1} ammonium chloride were added to a standard solution of 10^{-4} mol.L^{-1} ammonium chloride, thus maintaining the background concentration of ammonium ion throughout. When potassium ions were clearly seen to be interfering, aliquots of 10^{-4} mol.L^{-1} potassium chloride / 10^{-4} mol.L^{-1} ammonium chloride were added, thus reducing the overall concentration of potassium ion present in solution.

A decreased response to potassium ions was observed as the concentration of ammonium ions in the solution was diminished (figure 7). This showed that these ions did not remain in the membrane but ammonium, preferentially, set up equilibrium between the membrane and the electrolyte solution.

With time, the response of the ISE returned to the original value observed before the addition of ammonium interferent and the equilibrium position was reinstated.

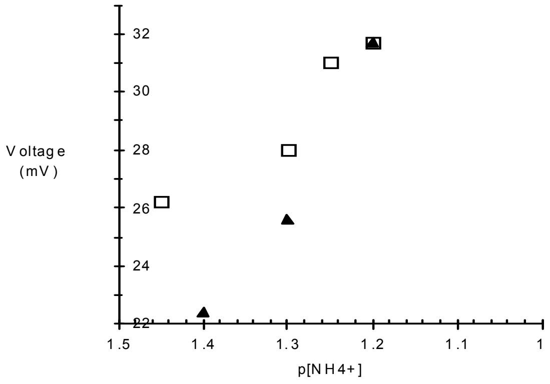


Figure 7. The variation in voltage with subsequent additions of potassium ions.

It would appear, therefore, that although potassium ions may act as interferent towards the ISEs, they do not remain in the membrane and were not responsible for the total electrode failure observed.

As there may be many unknown compounds present in the sample, it is possible that one of these was poisoning the electrode. A prime suspect of this poisoning effect must be phosphate. It is possible for phosphate ions entering the membrane due to a breakdown of the Donnan Exclusion Principle [14, 17].

IV. CONCLUSION

Rapid and reproducible analysis of fertilizers using ISEs based on other polymer than PVC is possible. The obtained device is shown to offer alternative solution, capable of satisfying the increasing demand for precise analytical information at lower cost through relatively simple instrumentation.

Pre-calibration was found to be necessary before analysis. Analysis using CVD method gave ammonium ion concentrations about 10 times higher than those determined experimentally using dip method and the manufacturer's values. This reinforced our previous claims that the CVD method must be used with care.

The composition of the calibration solution should match as close as possible that of the sample solution, otherwise large liquid junction potentials errors may occur. These variations in liquid junction arise due to large differences in ionic strength between calibrant and sample solutions, and it was believed to be true for the 2nd batch of fertilizers and calibration standards.

Potassium ions were shown to interfere reversibly, with $k_{NH4+, K+}$ of 7.4×10^{-2}, this is due to the similar ionic radius of the ammonium and potassium ions. This would explain, in part, the unexpectedly high ammonium concentrations determined in samples 4 to 6.

The "poisoning" effect of the ISEs was attributed to some unknown species, possibly an anion, in the fertilizer. Without a more detailed knowledge of the sample composition and subsequent testing, it is impossible to state definitely the interferent. Potassium ions were originally suspected as interfering, but the effect could not be repeated with potassium solutions. It is possible that the phosphates ions present in the fertilizer solution, which entered the membrane due to Donnan Exclusion Failure.

Further work should be carried out to ascertain the effect of phosphate ions on the ammonium selective membrane and to determine the selectivity of the membrane towards phosphate.

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