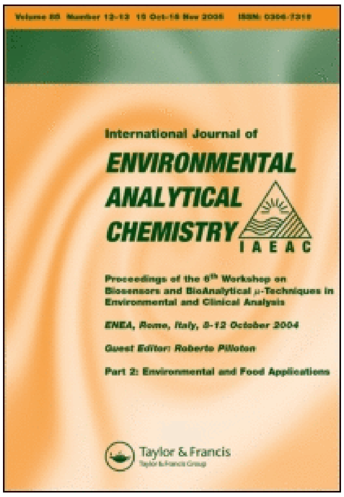

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Evaluation of a Gas-Phase Selective Electrode for the Quantitation of Ammonia in Liquid Piggery Wastes

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EVALUATION OF A GAS-PHASE SELECTIVE ELECTRODE FOR THE QUANTITATION OF AMMONIA IN LIQUID PIGGERY WASTES

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We evaluated a commercially available gas-sensing electrode for measuring the ammonia content of liquid piggery wastes (LPW). Samples previously acidified were analysed directly without purification or separation steps. The influence of metal ions, urea, volatile amines and suspended solids on electrode response was verified at concentration ranges generally encountered in LPW samples but no effects were observed. Reproducibility of measurements over the range 12.4–89.0 mM as ammonia was satisfactory (*cv* = ±5%) and recovered ammonia varied between 92% and 104%. Comparison of the electrode method to the standard distillation-titrimetric method yielded a close relationship as reflected by linear regression analysis on results ($m = 1.01 \pm 0.08$; $r = 0.997$). With adequate arrangements, one analyst could perform up to 200 samples per day.

KEY WORDS: Ammonia, selective electrode, liquid piggery wastes, metal ions, urea, suspended solids, volatile amines.

INTRODUCTION

Liquid piggery waste (LPW), with its daily production estimated to 35 million liters,[1] is an important agricultural by-product in the province of Québec. Disposal of LPW generally occurs by land spreading, but this procedure generates environmental problems (e.g. eutrophication of river waters) if the nutrient load greatly exceeds soil and crop requirements.[2] Thus, knowledge of the nutrient content of LPW is a prerequisite for prevention of the leaching of unadsorbed compounds to surrounding water. Among the major nutrients present in LPW, ammonia (i.e. ammonia gas: NH_3; plus ammonium ion: NH_4^+) is closely related to the soluble nitrogen content.[3] Therefore, its measure could provide a good estimate of the quantity of LPW to be applied relative to fertiliser nitrogen.

Difficulties may be encountered in determining the ammonia content of LPW if analytical methods are used without discrimination between samples from different sources. Indeed, LPW is a 95% watery solution containing urine, feces, food debris and contaminating materials from the animal living environment. It is characterized by wide ranges of organic and inorganic compounds, redox potentials, pH, colour, turbidity and high salt concentrations.[4] Among the methods available

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for ammonia analysis,[5-11] gas-sensing electrodes have proved to be reliable in determining ammonia in water and wastewaters,[8,12-14] and physiological samples.[15,16] Previous studies reported the utilisation of this electrode in anaerobic digests of swine wastes,[17] and animal slurries previously extracted with dilute acids.[18] However, investigations on the direct measurement of ammonia in LPW with the gas-sensing electrode have not been reported. Gas-sensing electrodes are characterized by a lack of responsiveness to colour, turbidity, and interfering substances, and are easy to use. We postulated, that they may constitute a good alternative to classical methods for laboratory and field use in our program.

In this study, we evaluated the characteristics of a commercially available ammonia gas-sensing electrode for response time, calibration range, stability and sources of bias in various aqueous mediums. The electrode was tested in LPW samples for accuracy and precision. Finally, our method was compared to the standard distillation-titrimetric method.[24] The results obtained in this preliminary study will subsequently be used for adapting the gas-sensing electrode method to a field scale.

EXPERIMENTAL

Apparatus and Material

The Orion ammonia gas-sensing electrode (Orion Res., Cambridge, MA), model 95-10, containing the Orion ammonia electrode solution (95-10-02) was employed. Potentiometric measurements were performed with an Orion 701A Digital Ionalyser pH-millivolt-meter. Ammonia probe and pH-millivolt-meter were calibrated as indicated by the manufacturer.[28]

Samples of LPW (0.5–1 L) were collected in polyethylene bottles and stored at 4 °C. Analysis were carried out within 3 days after collection. Aerated and fresh samples from various sources were used for their different ammonia content.

Reagents

All chemicals used were reagent grade. Ammonium chloride (Fisher Sci., Fairlawn, NJ) was heated overnight at 105 °C, and a 588 mM ammonia stock solution was prepared in 100 mM HCl and stored at 4 °C. Freshly prepared standards containing 3.0, 6.0, 30.0, 60.0, 90.0 and 120 mM as ammonia (NH_3) were prepared in 100 mM HCl before each batch analysis. A 10.0 M sodium hydroxide solution was prepared in deionized water and transfered to a polyethylene bottle for storage at room temperature. Stock solutions of $ZnCl_2$, $CuSO_4$, $MnCl_2$ and $Fe(NO_3)_3$ (Aldrich Chem., Milwaukee, WI) were prepared at 100 mM as the free metal in distilled and deionized water. A 4.0 mM urea solution (Aldrich, Chem., Milwaukee, WI) was prepared either in deionized water or 100 mM HCl. Table 1 lists the test mixtures used. The pH values of each of these mixtures is comparable to those encountered in LPW (5.2–8).[4] Mixture 2 was prepared according to Wong-Chong and Loher[26] with some modifications. Mixtures were stored in the dark at 4 °C. Rimini's reagent for primary amines[27] was prepared by diluting 2.0 mL of a

Table 1 Composition of test mixtures used for studying electrode response

Compound	*Mixture 1*	*Mixture 2*
	(*mM*)	
$NaNO_2$	8.9	8.9
KNO_3	9.0	9.0
NH_2CONH_2	4.5	8.3
$NH_2CH_2CO_2H$	8.9	3.3
NH_3 (as NH_4Cl)	44.0	37.0
$Na_2H_2PO_4$		15.7
K_2HPO_4		28.7
$MgSO_4 \cdot 7H_2O$		1.3
$FeCl_3$		0.07
$(NH_4)_6MO_7O_{24}$		0.05
NaCl		116
pH	5.7	7.4

5% w/v sodium nitroprusside-ethanol solution in 10.0 mL acetone. This solution was stored in the dark at 4 °C.

Procedure

Preparation of calibration curve All the standard solutions were brought to room temperature (±2 °C); 5.0 mL of the 3.0 mM standard solution was added to a 100 mL beaker containing 50.0 mL of deionized water and a PTFE-coated stirring magnet. The beaker was placed on a magnetic stirrer. The electrode was lowered to a depth of 2 cm and care was taken to avoid trapping air bubbles on the membrane. A gentle stirring was started and 1.0 mL of 10.0 M NaOH was added. Electrode potential was recorded after 1 minute. The same procedure was carried out for the other standard solutions in increasing order of ammonia concentrations (c.f. Reagents). Between each measurement the electrode was rinsed with deionized water and kept in alkaline 3.0 mM ammonia solution (prepared as above). If drift occurred during the calibration procedure, the electrode potential was restored to its initial value. A calibration curve was prepared by plotting the electrode potential measured for each standard solution against the respective ammonia concentration using semi-logarithmic graph paper. The slope of the calibration curve must be within ±2 mV of −56 mV at 21–23 °C.[28]

Measurement of ammonia in LPW LPW samples were brought to room temperature (±2 °C); 5.0 mL were diluted 1:1 with 200 mM HCl in caped polyethylene tubes (50 ml) and manually shaken for 2 minutes. Subsequently, 5.0 ml of this solution was added to a 100 ml beaker containing 50.0 ml of deionized water and a PTFE-coated stirring magnet. At this point, ammonia analysis was carried out as described for standard solutions. Potential values obtained were converted to ammonia concentrations with the calibration curve and corrected for dilution.

Sources of bias Various amounts of $ZnCl_2$ (Zn^{2+}: 1.41–2.42 mM), $CuSO_4$ (CU^{2+}: 1.21–2.94 mM), $MnCl_2$ (Mn^{2+}: 1.82–4.55 mM) and $Fe(NO_3)_3$ (Fe^{3+}: 1.79–17.9 mM) were mixed with ammonia standards and stored at 4 °C. Ammonia concentrations were determined 24 hours later. Test mixtures were used as described previously.

Volatile amines in LPW 10.0 mL of LPW were placed in a 25 mL beaker containing a PTFE-coated stirring bar and 0.5 mL of 10.0 M NaOH was added. The beaker was immediately covered with a filter paper soaked in Rimini's reagent and held in place with a glass evaporation dish. Colour development was allowed for 4 minutes under gentle stirring and heating. Total primary volatile amine concentrations were estimated by visual comparison with appropriate aqueous methylamine hydrochloride standards (Aldrich Chem., Milwaukee, WI) treated by the same procedure.

Total suspended solids (*TSS*) TSS content of LPW samples was determined according to Standard Methods.[24] Briefly, 10.0 ml of a well-mixed sample was diluted 1:1 with 200 mM HCl and filtered through a weighed 5.5 cm glass-fiber filter (934 AH, Whatman Ltd, Maidstone, England) placed in a Gooch crucible. The residue retained on the filter was dried to a constant weight at 104 °C (±1 °C) and the weight of the TSS residue was determined (weight of dried filter—initial weight of filter). The filtrate was collected and further analysed for ammonia content.

Reproducibility of measurements Two fresh LPW samples from different sources were used and each was divided into 5 equal subsamples. Ten determinations were carried out in each of the subsamples 1, 2 and 3 with the procedure previously described, while subsamples 4 and 5 were diluted 1:3 with 140 mM HCl and measured 6 times. Bartlett's test for homogeneity of variance and analysis of variance[31] were carried out at the $P \leqq 0.05$ level on results corrected for dilution. Duncan's multiple range test[31] was used where appropriate.

Recovery of ammonia in LPW Each of two fresh LPW samples from different sources were divided in 2 equal subsamples and stored in caped polyethylene tubes; 12 and 24 mM of ammonia as ammonium chloride was added to subsample 1, and 24 and 47 mM to subsample 2. After manual shaking for 2 minutes triplicate determinations were carried out on each subsample with the technique previously described. Results obtained were compared to the initial ammonia content of each subsample.

Comparison with the distillation technique Results obtained with the ammonia gas-sensing electrode on a series of LPW samples were compared to the distillation-titrimetric method according to Standard Methods.[24] In order to avoid interferences due to urea decomposition, distillation of LPW samples was carried out in an alkaline methyl alcohol solution under reduced pressure (4 kPa) at 40 °C.[25] Triplicate determinations were performed with the ammonia probe.

Triplicate titrimetric measurements were performed on the distillate of each sample. As a check for the method, distillation of test mixtures and LPW samples with various amounts of ammonia added as ammonium chloride showed quantitative recoveries between 84% and 118%. Relative standard deviation on three successive distillations was below 10%.

RESULTS AND DISCUSSION

The Orion 95–10 gas-phase ammonia electrode consists of a pH-Ag/AgCl combination electrode inserted in a cylindrical plastic tube. The tube is filled with a saturated ammonium picrate solution (50 mM).[19] The internal compartment is separated from the sample by a microporous gas-permeable membrane. Upon addition of 1.0 ml of 10 M NaOH to the sample, the lower pH of the internal electrolyte traps and convert ammonia gas to ammonium ions. The resulting variation in the concentration of ammonia changes the pH of the internal electrolyte which is sensed by the pH-Ag/AgCl electrode. The discriminating ability of the ammonia electrode is attributed to the microporous membrane which creates an air layer through which only neutral, gaseous species can diffuse. Therefore, compounds which change the internal electrolyte pH upon diffusion, interact with ammonia, or impede its diffusion through the gas-permeable membrane could preclude reliable quantitation of ammonia in LPW.

Response Time of the Electrode

Figure 1 shows the electrode potential against time after the addition of 1.0 mL of 10.0 M NaOH to ammonia standard samples. A steady electrode potential reading is attained within 30 seconds for ammonia concentrations above 6.0 mM, indicating rapid diffusion of ammonia across the microporous gas-permeable membrane. For lower concentrations, e.g. 3.0 mM, it is necessary to wait 50 seconds. Therefore, 1 minute was used as the standard response time after the addition of 1.0 mL of 10.0 M NaOH for ammonia concentrations over the range 3.0–120 mM.

Calibration Curve

According to the manufacturer,[28] the electrode is capable of measuring ammonia in aqueous solutions over the Nernstian range of 1.0 to 5×10^{-7} M with a mean standard deviation of ±2%. However, a calibration range between 3.0 mM and 120 mM was used in this study for measuring the ammonia content of LPW, which is well below 250 mM.[1,4] Electrode potential as a function of ammonia concentration was evaluated by calculating the terms in the regression equation: $y=(a+S_a)\log x+(b+S_b)$ where a and b are slope and intercept of the calibration curve and S_a and S_b are standard deviations of slope and intercept. The data

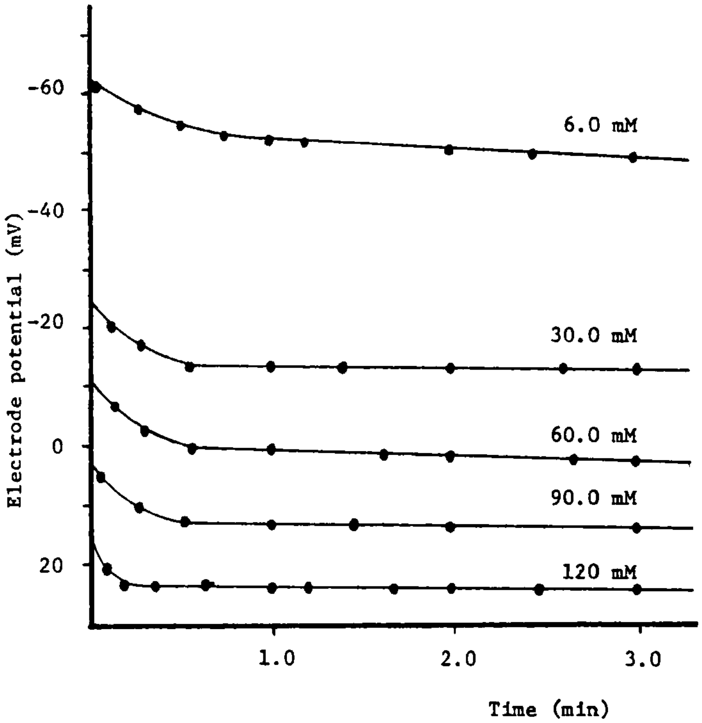

Figure 1 Electrode potential at various ammonia concentrations as a function of time.

yielded the following values for all terms: $a = 56.28\,\text{mV}$; $b = 103.10\,\text{mV}$; $S_a = 0.03\,\text{mV}$; $S_b = 0.02\,\text{mV}$; correlation coefficient was 0.9994.

Stability of Electrode Potential Readings

Figure 2 shows the variation of calibration curves measured over a 120 minutes period. Between each measurement the electrode was kept in an alkaline 3.0 mM ammonia standard sample without correcting for electrode potential drift. Major shifts (15–20 mV) to more negative values occurred at lower ammonia concentrations indicating poor recovery, even if between each calibration curve the electrode was kept for 45 minutes in the alkaline ammonia standard. This was due to residual ammonia left in the internal filling solution.[12] However, during LPW analysis we recalibrated the electrode after each 3 determinations with the alkaline 3.0 mM ammonia standard. A new calibration curve was established for each batch of LPW samples. When not in use, the electrode was soaked in 0.1 M citric acid buffer (pH 4.5) for 30 minutes[20] and kept in 0.1 M ammonium chloride solution.

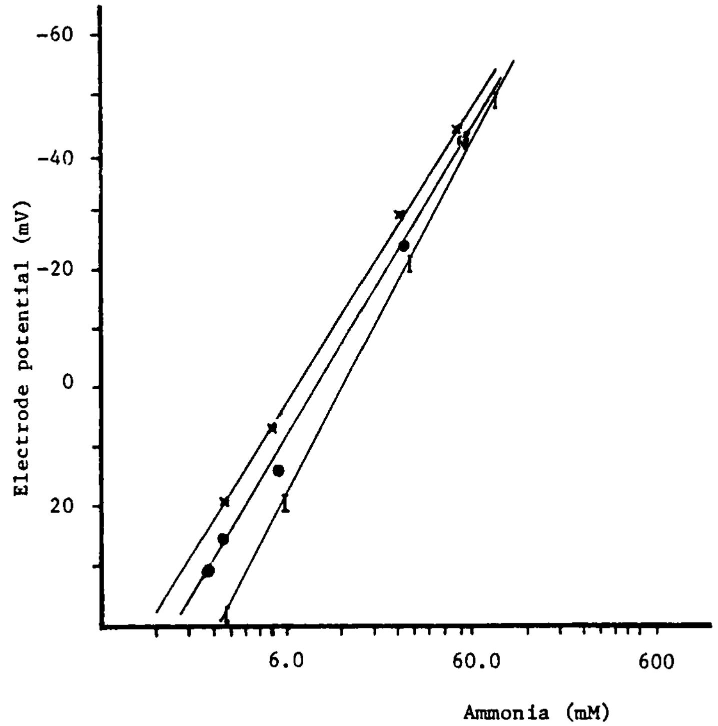

Figure 2 Electrode potential at various times as a function of ammonia concentrations.

Sources of Bias

Various physicochemical effects may interfere with the ammonia quantitation in LPW owing to the complexity of this medium.

Metal Ions

Ammonia (NH_3) can form soluble complexes with various metal ions with overall stability constants (pK) ranging from 2 to 19. Among these, we tested the presence of Mn^{2+}, Fe^{3+}, Zn^{2+} and Cu^{2+} on the electrode response to NH_3 at NH_3/M^{n+} ratios generally encountered in LPW samples. These results are summarized in Table 2. As expected, none of these metals ions produced low recoveries of ammonia because they form hydroxide precipitates in alkaline mediums with pK values well above those of ammonia complexes. The presence of a 2.0 mM mixture of these metals caused no observable effects on the determination of ammonia at concentrations of 15 and 59 mM (results not shown). Various NH_3/Fe^{3+} ratios ranging from 3 to 33 were used for testing the effect of hydrous ferric oxide on electrode response as this precipitate could prevent free diffusion of ammonia.[21] Again, no effect on ammonia recovery was observed (Table 2) for Fe^{3+} concent-

Table 2 Effects of metal ions on the response of the ammonia gas-sensing electrode

M^{n+}	*Ammonia*		*Recovery*	$[NH_3]/[M^{n+}]$
(mM)	*added*	*measured*[a] *(mM ± SD)*	(%)	
$MnCl_2$				
1.82	59	59 ± 1	100	32
4.55	88	85 ± 2	97	19
$CuSO_4$				
1.21	15	14.5 ± 0.3	97	12
2.94	29	29.4 ± 0.4	101	10
$ZnCl_2$				
1.41	15	14.6 ± 0.4	97	11
2.42	29	29.0 ± 0.6	100	12
$Fe(NO_3)_3$				
1.79	15	14.6 ± 0.3	97	8
	59	58 ± 1	98	33
3.58	15	14.7 ± 0.3	98	4
	59	56 ± 1	95	16
17.9	59	59 ± 1	100	3

[a] Mean and standard deviation on 3 determinations.

rations as high as 17.9 mM (1.0 g L^{-1}) in the presence of 59 mM NH_3 (1.0 g L^{-1}). These results indicate that Mn^{2+}, Cu^{2+}, Zn^{2+} and Fe^{3+} caused no observable effects on ammonia measurement at concentrations generally encountered in fresh and aerated LPW samples. Furthermore, other compounds present in test mixtures (Cl^-, SO_4^{2}, NO_3^-) did not affect electrode potential.

Urea

Urea interference on ammonia measurement was tested by measuring electrode response in either aqueous (pH 6.8) or 100 mM HCl urea standards over the range 2.1–8.4 mM. There was no effect on electrode potential as reported previously.[13,18–21]

Test Mixtures

Electrode response was tested in test mixtures containing various amounts of dissolved salts and nutrients. Dissolved salt concentrations in mixtures 1 and 2 were 137 mM and 490 mM respectively. Results in Table 3 show that when these samples were diluted 1:10 prior to ammonia determination, electrode response reflected ammonia content of mixture 2 while results obtained with mixture 1 were statistically comparable with the ammonia known value as assessed with the *t*-test

Table 3 Ammonia concentration measured in test mixtures with the gas-sensing electrode

	Ammonia		*Standard error*
	added	*measured*[a]	(%)
	(*mM* ± *SD*)		
Mixture 1	44	46 ± 1[b]	+4%
Mixture 2	37	37 ± 1	—

[a] Mean and standard deviation on 3 determinations.

[b] No significant difference with known value at 0.05 level (*t*-test).

Table 4 Ammonia concentration measured in filtrate and total LPW with the gas-sensing electrode

Total suspended solids	*Ammonia*[a]	
(% *dry matter*)	*LPW*	*Filtrate*
	(*mM* ± *SD*)	
LPW-1 3.2	52.4 ± 0.7	52.0 ± 0.6
LPW-2 3.2	53 ± 3[b]	53.5 ± 0.7

[a] Mean and standard deviation on 3 determinations.

[b] No significant difference between total and filtrate variances at $P \leq 0.05$ level with two-tailed *F*-test.

at $P \leq 0.05$ level. Furthermore, no major drift or recovery problems were experienced between measurements. These results suggest that: 1) salt concentrations up to 50 mM (1:10 dilution of 500 mM) cause no effects on electrode response. Indeed, a 1:10 dilution of our LPW samples should be adequate to prevent major osmolarity effects observed in other mediums containing high salt concentrations;[12] 2) despite the high range of salt concentrations encountered in LPW samples, the addition of 1.0 mL of 10.0 M NaOH to the sample should bring total ionic strength to 180–250 mM. This would eliminate major shifts between samples or with the internal filling solution which has an ionic strength of 400 mM.[12,19]

Total Suspended Solids (TSS)

Total solid content of LPW is quite low, accounting for 1–5% of the total weight.[1] A large fraction (10–35%) of total solids is composed of suspended solids. We tested the influence of this parameter on the ammonia determination in LPW as suspended solids could clog the membrane surface, slow the diffusion of liberated ammonia or even adsorb ammonium ions present at the pH of LPW (5.2–8).[4] Two fresh LPW samples of the same provenance were used and TSS content were determined (c.f. Experimental). Ammonia measurements were carried out either in the filtrate or in the total sample. Results shown in Table 4 indicate that no significant differences were observed for ammonia content in filtrates or total samples for the TSS content reported. As TSS content of other LPW samples was near the values reported in Table 4 (0.9–6.4%), subsequent ammonia determinations were performed on total LPW samples. Ammonia adsorption on suspended solids was tested by diluting LPW 1:1 either with 200 mM HCl or distilled and deionized water in caped polyethylene tubes. After manually shaking the tubes for 2 minutes[18] ammonia measurements were carried out. No significant differences (results not shown) were observed between the 200 mM HCl and aqueous dilutions on ammonia measurements. The same procedure applied to sedimented solids (10 000 g; 45 min.) gave similar results but ammonia content was negligible compared to LPW supernatant, indicating that ammonia is largely present as nonadsorbed ammonium ions. However, on long standing at room temperature (2 hrs), aqueous dilutions of LPW showed a net decrease of ammonia content owing to its volatilization in neutral to basic pH. This observation led us to dilute all LPW samples 1:1 with 200 mM HCl after bringing them to room temperature.

Volatile Amines

Interferences by dissolved volatile amines on the response of the gas-phase selective electrode for ammonia has been reported in the literature.[13,14] These substances diffuse through the microporous gas-permeable membrane and raise the internal electrolyte pH, thus generating erroneous responses of the ammonia probe.[22,23] Volatile amines are likely to be present in animal wastes, specially those kept in a reductive (anaerobic) environment.[29] However, concentrations of methylamine, ethylamine and dimethylamine have been reported to be 1–2% of total ammonia present in pig wastes, with primary amines being the main species.[30] Our results (not shown) confirmed these observations as maximum total primary amines concentrations measured in fresh and aerated LPW samples were lower than 1.3 mM (expressed as methylamine) for ammonia concentrations above the range 70–235 mM. Thus, volatile amine content of LPW is unlikely to interfere with ammonia determination as levels are within the standard error of the measurement.

Reproducibility of Measurements

Table 5 presents the results of ammonia determinations in 2 LPW samples of different sources analysed within 3 days after receipt. Subsamples 1, 2, 3, and subsamples 4, 5 were analysed 10 and 6 times respectively. No major differences were seen for results obtained either at 1:1 or 1:3 dilution. Values corrected for dilution gave comparable results. However, the lowest value obtained for subsample 3 of LPW-1 was statistically different from other results of the same LPW subsamples. Nevertheless, relative standard deviations were below 5% for ammonia concentrations over the range 12.4–89 mM. Comparable levels of reproducibility were obtained by other authors in complex samples of different origins using the same ammonia probe.[13–15,18] Relative total standard deviation for the

Table 5 Reproducibility of ammonia measurement in LPW with the gas-sensing electrode

Mean (*mM*)	*C.V.* (%)	*Mean corrected* (*mM*)
LPW-1		
25.3[a]	3.4	51
25.3[a]	3.3	51
23.5[a]	3.7	47[c]
12.4[b]	2.6	50
12.6[b]	4.4	50
LPW-2		
88[a]	2.2	177
87[a]	3.5	174
89[a]	3.8	177
44[b]	2.7	176
44[b]	2.1	174

[a] 10 determinations; samples diluted 1:1 with 200 mM HCl.
[b] 6 determinations: samples diluted 1:3 with 140 mM HCl.
[c] Statistically different from other values at $P \leq 0.05$ level (analysis of variance and Duncan's multiple range test).

Table 6 Recovery of ammonia in LPW as measured by the gas-sensing electrode

Ammonia initial (*mM* ± *SD*)	added	measured[a]	*Recovery* (%)
5.1 ± 0.1	12	16.9 ± 0.3	98.3
	24	28.8 ± 0.6	98.8
46 ± 1	24	68 ± 1	91.7
	47	95 ± 2	104

[a] Mean on 3 determinations.

ammonia concentration range studied in LPW gave an acceptable mean value of ±3.3%.

Recovery of Ammonia

Table 6 presents the results of recovered ammonia added to 2 LPW samples of different sources and different ammonia content. Recoveries were satisfactory showing quantitative recoveries between 92% and 104%. Overall recovery and confidence limit of the mean were 98.2% and 3.9% respectively ($P \leq 0.05$) for all the subsamples analysed ($n = 4$).

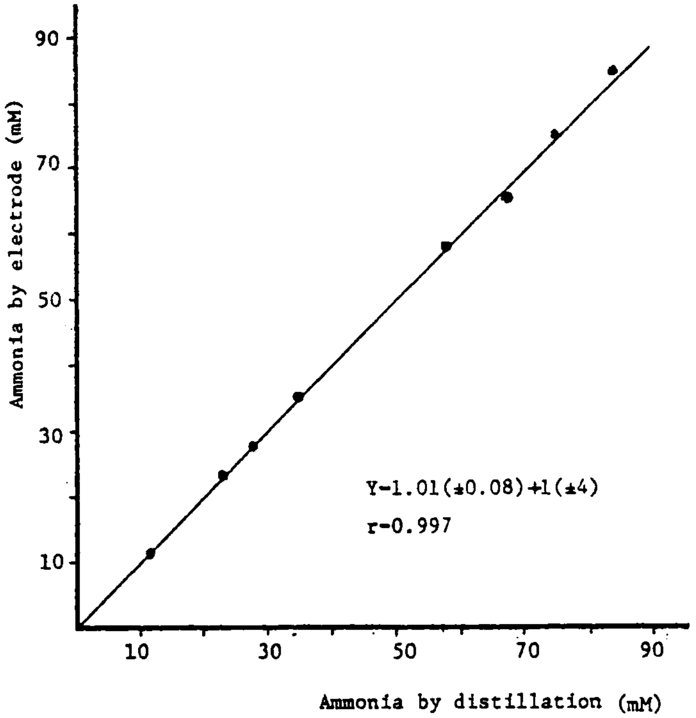

Figure 3 Correlation between determinations by gas-sensing electrode and distillation-titrimetric methods of ammonia in LPW samples ($n=8$).

Comparison Between Electrode and Distillation Methods

Fresh LPW samples containing different amounts of ammonia were analysed with the ammonia gas-sensing electrode and the distillation-titrimetric procedures. Regression analysis (Figure 3) indicates that there is an excellent linear correlation between methods over the concentration range studied. The confidence limits for the intercept and slope at $P \leq 0.05$ level were: $a=1 \pm 4$; $b=1.01 \pm 0.08$. The correlation coefficient was 0.997 ($n=8$). From this figure it is clear that the calculated slope and intercept did not differ significantly from ideal values of 1 and 0 respectively, and thus there was no evidence of systematic differences between the two sets of results. Furthermore, the relative differences calculated between each two sets of results gives a mean value of 3.4% (range: 0–8%) which are satisfactory for the concentration span verified.

CONCLUSION

The measurement of ammonia in LPW by an electrode method was rapid, accurate and cost-effective as compared to the widely used distillation and spectrophotometric techniques. Several parameters that could prevent reliable determination of ammonia in LPW were evaluated but none displayed observable effects on electrode response in the concentration range studied. Volatile amines and mercury are the only chemical species reported to interfere, but these compounds are unlikely to be present in LPW at interfering levels. A major advantage of using a gas-phase selective electrode for measuring ammonia in LPW is that no purification steps are required in order to compensate for large colour and turbidity gradients among samples of different sources and compositions. Finally, these results suggest that field measurements could be easily carried out with adapted equipment permitting rapid *in situ* analysis. This would eliminate ammonia variations during sampling and transport. With adequate arrangements one analyst could perform up to 200 samples per day.

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