Anion-selective membrane electrodes based on polymer-supported metalloporphyrins☆

Kum-Chul Oh [a], Kyung-A Kim [b], Insook Rhee Paeng [b], Dae-jin Baek [c], Ki-Jung Paeng [a],*

[a] *Department of Chemistry, Yonsei University, Wonju 220-710, South Korea*
[b] *Department of Chemistry, Seoul Women's University, Seoul 139-774, South Korea*
[c] *Department of Chemistry, Hanseo University, Seosan 352-820, South Korea*

Abstract

Prepared polystyrene pyridine copolymer supported manganese(III) protoporphyrin IX structures (MnPPIX-PSP4) were applied as an ionophore for ion selective electrodes. The responses of the solvent/polymeric membrane based on MnPPIX-PSP4 with standard PVC composition (NPOE as plasticizer: PVC: estimated ionophore in polymer = 132:66:2.6) were measured. The membranes based on MnPPIX-PSP4 exhibited not only excellent selectivity to iodide ion compared to other anions examined, but also Nernstian behavior (58 mV dec^{-1}). The optimization of the experimental conditions for potentiometric analysis offers a wide linear dynamic range (10^{-1} to 10^{-5} M I$^-$), reasonable detection limits ($\sim 10^{-5}$ M) and good durability within a limited error. The anion selective solvent/polymeric membranes based on polymer supported metalloporphyrins could overcome the shortcomings of limited life time, due to the loss of ionophores to the solution without effects from the high resistance of membranes. This is the first report that the addition of only around 1% of a polymer-attached ionophore into a plasticized PVC membrane leads to selectivity of salicylate due to the size exclusion effect. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Polymer supported manganese(III) protoporphyrin IX; PVC; Iodide ion-selective electrode; Lipophilic additive

1. Introduction

It is now well established that the use of metalloporphyrins as ionophores in solvent/polymeric membrane electrodes can induce potentiometric anion selectivity patterns that differ significantly from the classical 'Hofmeister' pattern ($ClO_4^- > I^- > Sal^- > NO_3^- > Br^- > Cl^- > OAc^- > SO_4^{2-}$) observed for membranes doped with typical quarternary ammonium type anion exchangers. Such non-Hofmeister selectivity has been ascribed to the selective axial ligation between the metal centers in the given metalloporphyrins and certain anions [1–8]. Electrode selectivity towards anions in these cases is not governed by anion lipophilicity as in the case of dissociated ion-exchanger, but by specific chemical interactions between the metalloporphyrins in the membrane and the anions in the sample solution, such as complex formation or coordination. The potentiometric behavior of these metalloporphyrin membranes towards anions is dependent upon the nature of the metal center, the porphyrin ring structure, the plasticizer, and the polymer matrix that holds these components.

These membranes, based on certain metalloporphyrins, which have been employed for carbonate or chloride measurements, respectively, exhibit much higher selectivity for salicylate over target anions. When such membrane electrodes are used for serum samples from patients taking aspirin, salicylate can produce a positive interference [2–4]. For many years,

---

researchers focused on reducing interference from lipophilic anions by changing the matrix, the nature of the metal that is incorporated into the porphyrin, the nature of the plasticizer and adding lipophilic anionic additives to the membrane composition. Recently, the use of asymmetric cellulose acetate type ion selective membranes has been described to minimize such salicylate interference problems, due to the size exclusion effect from polymer matrices [9,10].

Most of the metalloporphyrin plasticized membranes reported to date have been in a PVC matrix. However different selectivities and slopes can be observed when different matrices are used, such as a silicone rubber matrix or polyurethane. In particular, we reported that the selectivity of indium(III) octaethylporphyrin chloride [In(OEP)Cl] toward anions as a chloride sensor is enhanced in a silicone rubber membrane compared to a PVC membrane [8]. However, so far, an electrode with fully satisfactory selectivity and long term stability is not known yet, due to the leaching of the ionophores from the membrane [11].

In this experiment, we prepared the polymer-supported metalloporphyrin (polystyrene pyridine copolymer-supported manganese(III) porphyrin structure (MnP–PSP4)) and it was applied to an anion-selective electrode [12]. The potentiometric responses of the solvent/polymeric membrane based on MnP–PSP4 with standard PVC composition (NPOE as plasticizer: PVC: estimated ionophore in polymer = 66:33:1) were measured [8]. The membrane electrode prepared exhibited selective response to I^- without interference from Cl^- and salicylate. This electrode was applied successfully to measurement of I^- in spiked sea water samples.

2. Experimental

2.1. Reagents

Poly(vinyl chloride), *o*-nitrophenyl octyl ether (NPOE) and tridodecylmethylammonium chloride (TDMACl) were purchased from Fluka (Ronkonkoma, NY). Protoporphyrin IX (PPIX), 4-vinylpyridine, styrene and α,α′-azobisisobutyronitrile (AIBN) were purchased from Aldrich (Milwaukee, USA). The styrene was washed with aqueous NaOH to remove inhibitors, then with water, dried with $MgSO_4$ and distilled under reduced pressure, and passed through a neutral alumina column before use. AIBN was crystallized from acetone and dried under a vacuum at room temperature. All other chemicals including the sodium salts of the anions examined were of analytical reagent grade and used without further purification. Standard solutions and buffers were prepared using deionized water.

2.2. Syntheses of polymer supports

The polymer support, poly(4-vinylpyridine-co-styrene) (PSP4), was prepared using a known method [12]. A typical procedure for PSP4 is described as follows: 3.47 ml (0.03 mol) of freshly distilled styrene, 7.86 ml (0.07 mol) of 4-vinylpyridine and 0.3 g (2 mmol) of AIBN were placed in a Schlenk tube and dissolved in 20 ml of benzene. The mixture was degassed via five freeze-pump-thaw cycles in a vacuum line, and reacted at 60°C for 24 h under a nitrogen atmosphere and cooled to room temperature. The reaction mixture was then poured into petroleum ether and the precipitated polymer was filtered, recrystallized from chloroform + petroleum ether, then dried in vacuo to yield the yellowish polymer.

2.3. Syntheses of polymer-supported MnPPIXs (MnPPIX-PSP4)

Protoporphyrin IX was purchased from Aldrich. Mn (III) was inserted into the plain porphyrin PPIX according to a standard method [12,13]. MnPPIX (50 mg) $(7.7 \times 10^{-5}$ mol$)$ and 2 ml of thionyl chloride ($SOCl_2$, 2.7×10^{-2} mol) were combined in a 250-ml round bottom flask. When gas evolution subsided, 50 ml of 1,1,2,2-tetrachloroethane and 3 g of polymer PSP4 $(2.9 \times 10^{-2}$ mol of repeating polymer units) were added. The mixture was heated to 130°C while stirring to drive off excessive $SOCl_2$. After cooling to 10°C, 2 g of $AlCl_3$ was added, and the mixture was stirred without further cooling, for 24 h. The solid was filtered, washed thoroughly with tetrachloroethane and recrystalized in methanol. The final product was identified using an infrared spectrophotometer (Midac, IR spectrum was reported in Ref. [12]). The structure of the final product is given in Fig. 1. The amounts of attached metalloporphyrin were estimated by determining the amount of manganese in the metalloporphyrin. Manganese was extracted by the minimum amount of concentrated H_2SO_4 and diluted to 100 ml with deionized water. The amounts of extracted manganese were determined by atomic absorption spectroscopy (Perkin-Elmer) using a calibration method. The estimated amounts of metalloporphyrin ranged from 13.0 to 15.0 wt.% of the total weight of the polymer-supported metalloporphyrin (average 14.0%).

2.4. Preparation and evaluation of polymer membranes and electrode

PVC matrix membranes were prepared according to the method reported previously [14]. The composition of the PVC-based anion-selective membrane was 1 wt.% of estimated ionophore, 33 wt.% PVC and 66 wt.% plasticizer in a total weight of 200 mg. The real
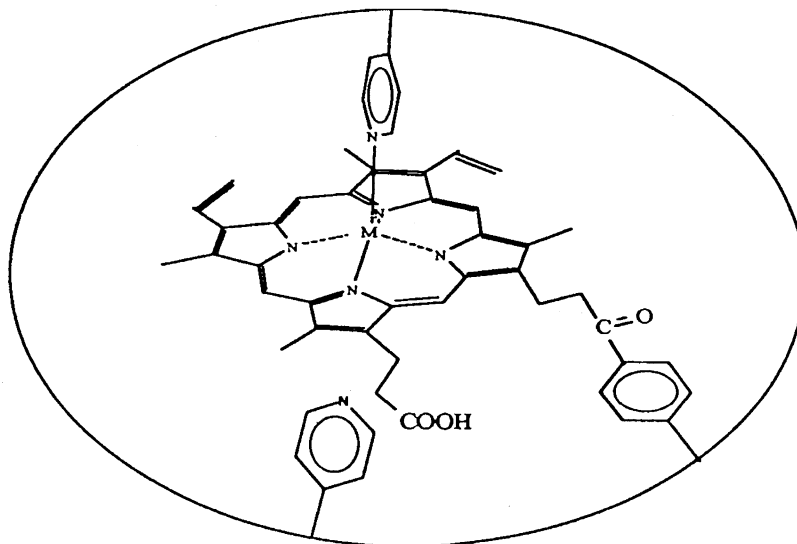
Fig. 1. The structure of polystyrene pyridine copolymer supported manganese (III) protoporphyrin IX.

total weight of prepared membrane was about 200.6 mg, because the weight of the estimated ionophore was not included the polymer. The detailed compositions of membranes used in this experiment are listed in Table 1. The polymer containing more than 14% (wt./wt.%) of metalloporphyrin was chosen as an ionophore. The membranes were prepared by dissolving the mixture in 5 ml THF. In each case, after curing, small disks (5.5 mm) were punched from the cast films and mounted in Philips electrode bodies (IS-561; Glasblaserei Muller, Zurich, Switzerland).

The potentiometric behavior of the membrane electrodes was evaluated using the conventional ISE configuration. For all electrodes, a mixture of 0.1 M NaCl was employed as the internal filling solution. The external reference electrode was an Orion sleeve-type double junction Ag | AgCl electrode (Model 90-02). The electrodes were connected through a high impedance amplifier to an IBM AT-type computer equipped with an analog-to-digital converter. The cell potential was measured at ambient temperature (22°C) by immersing the ISEs and the reference electrode into a beaker containing 200 ml of universal buffer (11.4 mM boric acid; 6.7 mM citric acid; 10.0 mM sodium dihydrogen phosphate, pH 5.5). The calibration data were obtained from additions of standard solutions. The solutions were stirred magnetically throughout and equilibrium potentials were recorded. Selectivity coefficients were estimated according to the separated solution method at an interfering anion concentration of 0.1 M [15]. The detection limits of the membrane electrodes were obtained from the calibration plots following the recommended procedure [16]. The response of an electrode toward pH was obtained by titrating a universal buffer of pH 2.8 with small aliquots of LiOH, while simultaneously monitoring the pH of the sample solution with a combination glass pH electrode.

3. Results and discussion

Previous studies showed that porphyrins containing either Mn(III) exhibit high chloride selectivity, deviating from the Hofmeister series [2,5,8]. However, the use of solvent polymeric membranes based on those ion carriers has been limited due to their response to lipophilic anions, particularly to salicylate.

The purpose of making polymer-supported metalloporphyrin is not only to decrease the leaching of ionophore from polymer matrices without losing too much of the hydrophilicity of the ionophore, but also to reduce salicylate interference as a result of the size

Table 1
The compositions of anion-selective membranes

Membrane	1	2	3	4
Ionophore (1 wt.%)	MnP[a]	PSP4[b]	MnP–PSP4[c]	MnP–PSP4
Matrix (33 wt.%)	PVC[d]	PVC	PVC	PVC
Plasticizer (66 wt.%)	NPOE[e]	NPOE	NPOE	NPOE
Lipophilic additive (50 mol%)	None	None	None	TDMACl[f]

[a] Manganese (III) porphyrin.
[b] Polystyrene pyridine.
[c] Polystyrene pyridine copolymer supported manganese (III) porphyrin structure.
[d] Poly(vinyl chloride) high molecular weight.
[e] 2-Nitrophenyl octyl ether.
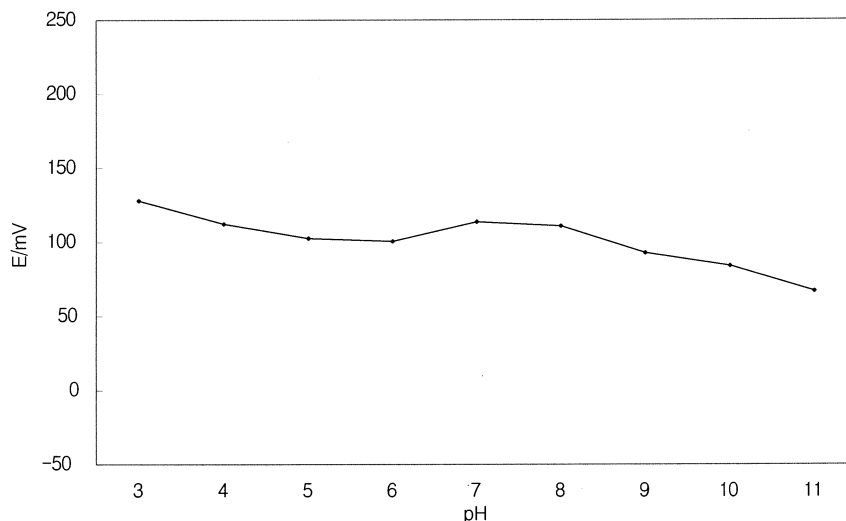[f] Tridodecylmethylammonium chloride.

Fig. 2. pH response of the polystyrene pyridine copolymer supported manganese (III) protoporphyrin IX-based membrane electrode.

exclusion from highly folded polymer matrices like the asymmetric membrane. Furthermore, it can remove the super-Nernstian behavior observed with InOEPCl by Park et al. [4] by decreasing the association of porphyrin to form dimers and it is useful for studying migration phenomena of ions in polymer matrices if this system is applied successfully. The choice of the ionophore chemically bonded to the polymer matrix to overcome these problems was not an easy task because most of the polymer membranes that contain an ionophore exhibited very high resistance. Thus we added the pyridine functional group to the polystyrene backbone to enhance the solubility in THF solvent and to reduce the resistance. The membrane with the 5,10,15,20-tetrakis (4-carboxyl phenyl porphyrinato) manganese (III) chloride covalently attached to the polymer showed severe cationic interference over levels of 10^{-2} M of cations and was hardly soluble in THF. Thus we chose MnPPIX instead of tetraphenylporphyrin manganese chloride (MnTPPCl).

The pH response profile for the MnPPIX-PSP4-based electrode was examined by use of 10^{-3} M NaI solution, adjusted with LiOH as an alkaline medium and is shown in Fig. 2. The working buffer (universal buffer, pH 5.5) was employed throughout the experiment, because the emf of the prepared membranes gives the lowest value at pH 5.5, even though the membrane shows little response to pH in the pH range of 3–11.

The static response characteristics of metalloporphyrin and polymer-based anion-selective PVC membranes are listed in Table 2. Because we employed a buffer system throughout this experiment, we were not concerned with the pH response of blank polymer and blank porphyrin. Since the polymer (PSP4) employed in this study did not exhibit any response to any anions and cations we examined, we can examine their poten-

tiometric behavior either with the metalloporphyrin polymer supported or not. It is noticeable that the MnPPIX-based membrane did not exhibit a significant response to any anions, while the same porphyrin with polymer supported (PSP4)-based membrane exhibited an appreciable slope (-58.5 mV/pI$^-$) with a straight line between 10^{-1} and 10^{-5} M NaI. The detection limit is below the 10^{-5} M level under optimum conditions with MnPPIX-PSP4 as the iodide ion sensor (Fig. 3). The absence of emf response observed from the blank MnPPIX membrane is a little surprising, however it may be caused by severe leaching into the solution and/or the cation response due to free carboxyl groups of the porphyrin cancels out the anion response from ligation reactions with the metal center.

In general the total response toward a given anion is likely to depend on its relative strength as an axial ligand (e.g. association constant at 6th coordination site). However, the selectivity pattern (Table 3) of the MnPPIX-PSP4-based membrane exhibits good agreement with the Hofmeister series except for salicylate ion. The early report by Meyerhoff et al. indicated that when one side of the Mn(III) porphyrin is totally blocked (capped) with an intermolecularly bound neutral axial ligand selectivity it essentially reverts back to the classical Hofmeister pattern [2]. It is well defined that imidazole and pyridine are strong σ electron donating ligands and such strong intermolecular coordination on one side of the metal generally weakens the interactions of ligands at the other axial site [17]. The pyridine bound to styrene polymer backbones play an important role in blocking the other side of the MnPPIX as shown in Fig. 1. Thus, within the membrane phase, the small ions like chloride ions are likely to be dissociated from such a porphyrin structure yielding a positively charged lipophilic ion-exchange type species.

Table 2
Potentiometric performances of manganese porphyrin, base polymer and polymer-supported manganese porphyrin-based membranes

Ionophore	Slope/mV dec^{-1}	Selectivity coefficient log $K^{pot}_{I-,j}$								Detection limit log [c/M]
		Br$^-$	Cl$^-$	ClO$_4^-$	NO$_2^-$	NO$_3^-$	Oac^{-a}	Sal^{-b}	SO$_4^{2-}$	
MnP	13.0	-0.8	-0.8	-0.1	-0.7	-0.7	-0.1	0.2	-1.2	-3.00
PSP4	–	No response	No response	No response	No response	No response	No response	No response	No response	No response
MnP–PSP4	58.5	-2.1	-3.6	1.16	-2.4	-1.3	-4.3		-4.3	-5.51
MnP–PSP4 + additive	56.0	-2.2	-3.7	1.3	-2.5	-1.4	-4.5		-4.5	-5.32

^{a} Acetate.
^{b} Salicylate.

Consequently, analyte anions can enter the membrane phase predominantly as solvated counter ions with little or no affinity for the central Mn(III) atom. For that reason, we can expect that the relatively bigger salicylate ion could not penetrate the membrane phase properly, and would give a poor response to the aforementioned membrane, because of the size exclusion effect from the folded polymer matrix. However, the response to salicylate was dramatically enhanced with addition of a cationic lipophilic additive to the membrane (Table 3). This is associated with the fact that the mobility of lipophilic anions such as salicylate is enhanced with addition of a lipophilic additive [18]. Structural information regarding the polymer supported metalloporphyrin employed in this experiment is subject to a further study by us. However, the reason for good selectivity toward iodide over salicylate by the electrode based on the polymer supported metalloporphyrin is the size exclusion effect. The major point of this paper is that it is the first work in which it can be claimed that addition of only around 1% of a polymer-attached ionophore into a plasticized PVC membrane leads to this size exclusion effect.

To demonstrate the usefulness of the MnPPIX-PSP4 based membrane for environmental analysis, its potentiometric response to 10^{-3} M I$^-$ which is spiked to real seawater has been investigated. The results are listed in Table 3. Seawater samples were taken at the west side of Sochung Island, which is located in an uncontaminated area of the Yellow Sea. The concentration measured from I$^-$ spiked sea water samples by the prepared electrodes showed very good agreement with the spiked concentration. This result means the presence of chloride ions of 0.5 M (in sea water) does not change the response of the electrode to iodide ion significantly, resulting in similar values within the required accuracy (relative error, 0.8%) and precision (RSD, 0.6%) of our experimental set up. Furthermore, one membrane can be used for more than 6 months under laboratory conditions, if it is properly stored (dipped in water) and cross contamination is avoided.

4. Conclusions

In summary, MnPPIX-PSP4-based anion-selective PVC membrane electrode can be used as an iodide sensor, because the membranes based on MnPPIX-PSP4 exhibit not only excellent selectivity to iodide ion with respect to other anions examined, but also Nernstian behavior (-58 mV dec^{-1}). The optimization of experimental conditions for potentiometric analysis offers a wide linear dynamic range (10^{-1} to 10^{-5} M I$^-$), reasonable detection limits (10^{-5} M)
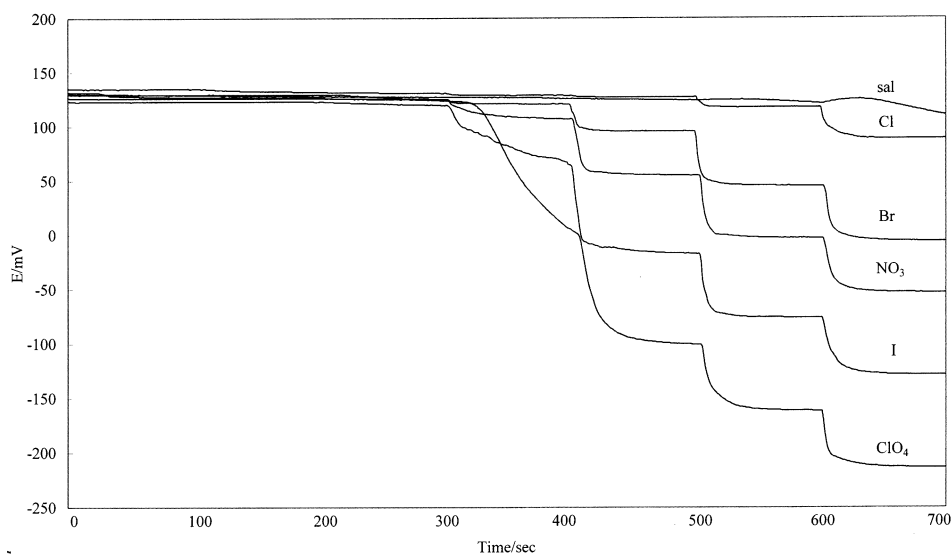
Fig. 3. Dynamic responses of the anion selective electrode based on polymer supported manganese porphyrin to various anions.

Table 3
The analytical results of I^- spiked in real seawater by an iodide ion-selective electrode based on polystyrene pyridine copolymer supported manganese(III) protoporphyrin IX

Sample number	10^{-3} M I^- spike
1	0.998
2	0.991
3	0.998
4	0.984
5	0.991
$\bar{X}$	0.992
RSD	0.6%

and good durability within a limited error range. Even though this experiment focused on the iodide ion sensor, this membrane electrode can be applied to perchlorate or nitrate sensors depending on the matrix, and the membrane with a lipophilic additive can be applied as a salicylate sensor.

Acknowledgements

References

[1] F. Hofmeister, Arch. Exp. Pathol. Pharmakol. 24 (1888) 247.
[2] N.A. Chanitotakis, A.M. Chasser, M.E. Meyerhoff, J.T. Groves, Anal. Chem. 60 (1988) 185.
[3] M. Huser, W.E. Morf, K. Fluri, K. Seiler, P. Schulthess, W. Simon, Helv. Chim. Acta 73 (1990) 1481.
[4] S.B. Park, W. Matuszewski, M.E. Meyerhoff, Y.H. Liu, K.M. Kadish, Electroanalysis 3 (1991) 909.
[5] A. Jyo, H. Egawa, Anal. Sci. 8 (1992) 823.
[6] E. Bakker, E. Malinowska, R.D. Schiller, M.E. Meyerhoff, Talanta 41 (1994) 881.
[7] E. Malinowska, M.E. Meyerhoff, Anal. Chim. Acta 300 (1995) 33.
[8] I.J. Yoon, J.-H. Shin, I.R. Paeng, H. Nam, G.S. Cha, K.-J. Paeng, Anal. Chim. Acta 367 (1998) 175.
[9] K.S. Lee, J.H. Shin, S.H. Han, G.S. Cha, D.S. Shin, H.D. Kim, Anal. Chem. 65 (1993) 3151.
[10] M.J. Cha, J.H. Shin, B.K. Oh, C.Y. Kim, G.S. Cha, D.S. Shin, B. Kim, Anal. Chim. Acta 315 (1995) 311.
[11] E. Bakker, P. Buhlmann, E. Pretsch, Chem. Rev. 97 (1997) 3083.
[12] J.Y. Shin, K.-A Kim, H.G. Kim, I.R. Paeng, D.-G. Kim, K.-J. Paeng, Bull. Kor. Chem. Soc. 19 (1998) 875.
[13] L.D. Rollman, J. Am. Chem. Soc. 97 (1975) 2132.
[14] J.S. Bradshaw, R.M. Izatt, Z. Yan, Chem. Rev. 94 (1994) 939.
[15] P. Schulthess, D. Ammann, W. Simon, C. Caderas, R. Stepanek, B. Krautler, Helv. Chim. Acta 67 (1984) 1026.
[16] IUPAC Recommendation for Nomenclature of Ion-Selective Electrodes, Pure. Appl. Chem. 66 (1994) 2527.
[17] S.L. Kelly, K.M. Kadish, Inorg. Chem. 21 (1982) 3631.
[18] G.S. Cha, H. Nam, personal communication, Kwangwoon University, South Korea.