

A PVC Plasticized Sensor for Ni(II) Ion Based on a Simple Ethylenediamine Derivative

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A new PVC membrane ion selective electrode which is highly selective towards Ni(II) ions was constructed using a Schiff base containing a binaphthyl moiety as the ionophore. The sensor exhibited a good Nernstian response for nickel ions over the concentration range $1.0 \times 10^{-1} - 5.0 \times 10^{-6}$ M with a lower limit of detection of 1.3×10^{-6} M. It has a fast response time and can be used for a period of 4 months with a good reproducibility. The sensor is suitable for use in aqueous solutions in a wide pH range of 3.6–7.4 and works satisfactorily in the presence of 25% (v/v) methanol or ethanol. The sensor shows high selectivity to nickel ions over a wide variety of cations. It has been successfully used as an indicator electrode in the potentiometric titration of nickel ions against EDTA and also for the direct determination of nickel content in real samples: effluent samples, chocolates and hydrogenated oils.

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Introduction

There has been a profound development in potentiometric sensors over the past 3–4 decades, mainly thanks to their use in many fields like agriculture, industry, environment and pharmacy. The need for developing a sensor that is fast, accurate, reproducible and above all, selective to the ion of interest is the main reason for the quantum leap. The major challenge of research in this field has been in designing and subsequent syntheses of the different types of ionophores and this has been the thrust area of research.^{1,2}

Nickel monitoring has become quite essential mainly due to the material's toxic nature. It is a potent carcinogen and it causes acute pneumonitis, dermatitis, asthma, and nasal and lung cancer.^{3,4} Nickel is present at low concentrations in hydrogenated oils, milk, and milk products and also in electroplating effluents. The conventional methods, such as the gravimetric method using dimethylglyoxime⁵ or the spectrophotometric method,⁶ are not only time consuming but also have some practical inconveniences. Though a number of ion selective electrodes are reported in the literature,^{7–15} most of them are associated with one or other drawbacks like poor selectivity, narrow concentration range, non-Nernstian response, relatively long response time or poor reproducibility.

In continuation to our work on metal analyses at trace levels,^{16,17} this paper presents the fabrication of a PVC matrix membrane sensor incorporating a Schiff base as ionophore and its use in the determination of Ni(II). The proposed sensor could be effectively applied for direct determination of nickel content in real samples.

Experimental

Reagents

All the reagents used were of analytical reagent grade. Dioctyl phthalate (DOP), dioctyl sebacate (DOS), dioctyl adipate (DOA), dimethyl sebacate (DMS), dibutyl phthalate (DBP) and sodium tetraphenylborate (NaTPB) were obtained from Lancaster (UK) and were used without any further purification. The metal salts, high relative molecular weight PVC, tetrakis[3,4-bis(trifluoromethyl)phenyl]borate and dibutyl sebacate (DBS) were purchased from Merck and used without any further purification. Tetrahydrofuran (THF) and oleic acid was purchased from S. D. Fine Chem, India and was distilled before use. The ionophore, *N*¹,*N*²-bis((naphthalen-1-yl)methylene)ethane-1,2-diamine (NED), was synthesized and purified as described elsewhere (Fig. 1).¹⁸ All the metal salt solutions were prepared in doubly distilled water and solutions of different concentrations were made by serial dilution of the 0.1 M stock solutions.

Electrode preparation

A mixture of PVC, plasticizer (DOP) and the anion excluder (NaTPB) in the ratio 31:65:2 (w/w%) was dissolved in 5–7 mL of THF. To this mixture, the ionophore (2%) was added and the solution was mixed well. It was then poured into a petri dish

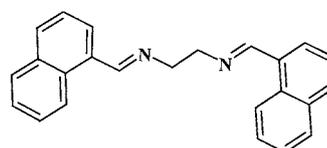


Fig. 1 Structure of NED.

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Table 1 Optimization of membrane ingredients

| Sensor | Composition of each membrane, w/w% | | | | Working concentration range/M | Slope/mV decade of activity ⁻¹ (± 1.0) ^a | Response time/s |
|--------|------------------------------------|-----|-------------|-------|---|--|-----------------|
| | PVC | NED | Plasticizer | NaTPB | | | |
| A | 96 | 2 | 0 | 2 | $1.0 \times 10^{-1} - 1.0 \times 10^{-5}$ | 21.7 | 65 |
| B | 31 | 2 | DOP, 65 | 2 | $1.0 \times 10^{-1} - 1.3 \times 10^{-6}$ | 29.9 | 15 |
| C | 31 | 5 | DOP, 62 | 2 | $1.0 \times 10^{-1} - 5.5 \times 10^{-6}$ | 28.2 | 20 |
| D | 31 | 7 | DOP, 60 | 2 | $1.0 \times 10^{-1} - 6.3 \times 10^{-6}$ | 27.6 | 20 |
| E | 31 | 2 | DBP, 65 | 2 | $1.0 \times 10^{-1} - 9.9 \times 10^{-5}$ | 17.5 | 40 |
| F | 31 | 2 | DOA, 65 | 2 | $1.0 \times 10^{-1} - 4.2 \times 10^{-5}$ | 20.7 | 40 |
| G | 31 | 2 | DMS, 65 | 2 | $1.0 \times 10^{-1} - 8.3 \times 10^{-4}$ | 15.8 | 30 |
| H | 31 | 2 | DBS, 65 | 2 | $1.0 \times 10^{-1} - 1.0 \times 10^{-4}$ | 14.9 | 25 |
| I | 31 | 2 | DOS, 65 | 2 | $1.0 \times 10^{-1} - 2.2 \times 10^{-4}$ | 12.3 | 30 |

a. RSDs based on three replicates.

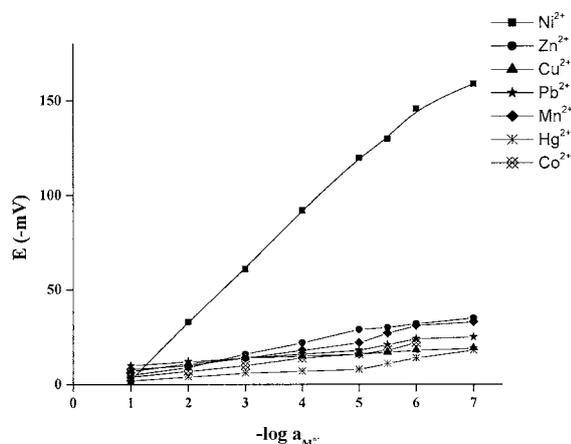
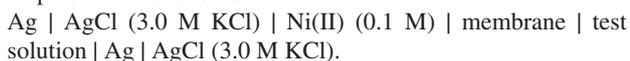


Fig. 2 Potential response of various sensors based on NED. Conditions: composition ratio, 31:2:65:2 (PVC:NED:DOP:NaTPB) (wt%); internal solution, 1.0×10^{-1} M of each cation used; conditioning in 1.0×10^{-1} M of corresponding cation salt solution for 24 h.

and allowed to evaporate for 24 h. Small disk shaped membranes were cut out and glued to one end of a hollow Pyrex glass tube using Araldite. The membrane was conditioned by dipping it in a 1.0×10^{-1} M nickel nitrate solution for 24 h.

Potential measurement and calibration

Potentials were measured at ambient temperature ($25 \pm 0.1^\circ\text{C}$) on a Systronics digital ion meter. An Ag/AgCl reference electrode was used in conjunction with the developed Ni(II) sensor. The cell assembly for potentiometric measurements can be represented as follows:



The performance of the developed Ni(II) sensor was investigated by measuring the potential in Ni(II) solutions prepared in the concentration range $1.0 \times 10^{-1} - 1.0 \times 10^{-7}$ M. The solutions were stirred and the stable potential reading was taken.

Preparation of chocolate and edible oil samples

Ten grams of chocolate sample were heated in a silica crucible at 400°C on an electric bunsen burner until ash is obtained. The residue was dissolved in 2 mL conc. HNO_3 and again heated at 350°C for 2 h; the process was repeated till no traces of carbon are left. The final residue was treated with 0.5 mL conc. HCl and 1–2 mL 70% perchloric acid and then evaporated to fumes. The solid residue was dissolved in water,

filtered and then transferred quantitatively to a 100 mL volumetric flask. The pH was adjusted to 5.0 by adding 10 mL of buffer solution (0.1 M potassium hydrogen phthalate/NaOH) and then the solution was quantitatively diluted.

Ten grams of the hydrogenated edible oil (Dalda) were heated at 500°C for 1 h. The residue was completely dissolved in 5 mL of 0.1 M HNO_3 . The solution was then transferred into a 100 mL volumetric flask; the pH was adjusted to 5.0 by adding 10 mL of buffer solution (0.1 M potassium hydrogen phthalate/NaOH) and then the solution was quantitatively diluted. The nickel content determined with the developed sensor was compared with the result obtained using the ICP technique on a Thermo Elemental, IRIS INTREPID II XSP DUO.

Results and Discussion

The ionophore that is incorporated into the PVC matrix is the electroactive species that selectively binds to the particular ion of interest. The potential response can be attributed to the ion-exchange process at the membrane-sample interface. The potential responses of the most sensitive sensors prepared under the same experimental conditions are shown in Fig. 2. Among the different metal ions tested, Ni(II) showed a Nernstian response while the others were non-Nernstian.

The optimum membrane composition was determined and this membrane was then used for testing the membrane characteristics.

Effect of membrane compositions

A number of membrane compositions were investigated by varying the ratio of plasticizers and the ionophore and the results are given in Table 1. In neutral carrier membranes, plasticizers that are compatible with the ionophore provide a smooth surface to the membrane and hence enhance the response characteristics.¹⁹ A membrane without plasticizer was first prepared and its effect was initially studied (sensor A). The nature of the plasticizer influences the dielectric constant and the mobility of the ions in the membrane. These membrane solvents are seen to strongly influence the working concentration range and the slope of the sensor. It was observed that the sensor B with DOP as plasticizer was found to give the best response in terms of the slope and the concentration range. The slopes in the case of the sebacates and adipates are sub-Nernstian. The potentiometric response of the sensor towards Ni(II) ions is found to be dependent on the concentration of the ionophore used. Different compositions (w/w%) of the

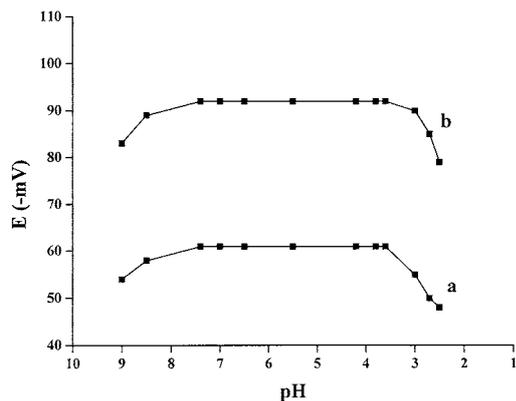


Fig. 3 Effect of pH on the cell potential of the developed sensor at 1.0×10^{-3} M (a) and 1.0×10^{-4} M (b).

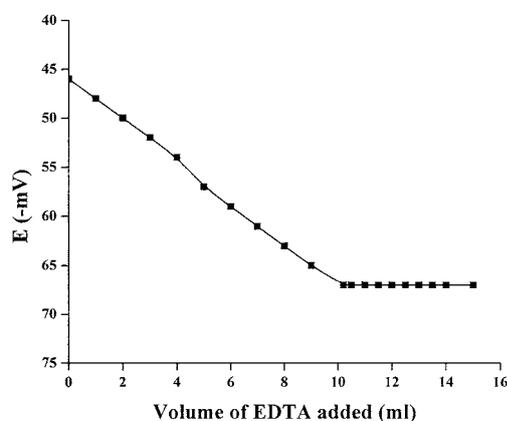


Fig. 4 Potentiometric titration curve of 20.0 mL of 5.0×10^{-3} M Ni(II) solution with 1.0×10^{-2} M EDTA using the developed sensor as an indicator electrode.

ionophore were also tried to obtain the right composition of ionophore that gives the best response characteristics. The maximum sensitivity was observed for 2% (w/w) of the ionophore. On increasing the ionophore content, the slopes are affected; this may be related to the change in the water uptake capacity of the membrane.

The effect of the anionic excluders was also studied. Anionic excluders are beneficial as they contain ionic sites with a charge sign opposite to that of the primary ion and thus improve the Nernstian response of the sensor.²⁰⁻²³ These lipophilic excluders help in reducing the membrane resistance,²⁴ improving the selectivity²⁵⁻²⁷ and reducing the interference from sample anions.^{28,29} There is a great improvement in the potentiometric response on the addition of the anionic excluder, NaTPB (2 wt%) while the others, tetrakis[3,4-bis(trifluoromethyl)phenyl]borate and oleic acid gave a sub-Nernstian response.

Thus, the best composition was found to be 31:2:65:2 (PVC:NED:DOP:NaTPB). And it gave a Nernstian slope of 29.9 ± 1.0 mV per decade of activity for the concentration range 1.0×10^{-1} – 5.0×10^{-6} M. The detection limit was calculated from the graph by the intersection of the two extrapolated linear segments of the calibration plot and was found to be 1.3×10^{-6} M.

Response and lifetime

The response time of the Ni(II) sensor, which is the average time for the sensor to reach a potential within ± 1 mV of its final

Table 2 Effect of partially non-aqueous medium on the working of the developed sensor

| Non-aqueous content, % v/v | Slope/mV decade of activity ⁻¹ | Working concentration range/M |
|----------------------------|---|---|
| 0 | 29.9 | 1.0×10^{-1} – 1.3×10^{-6} |
| Ethanol | | |
| 10 | 29.3 | 1.0×10^{-1} – 5.2×10^{-6} |
| 25 | 29.1 | 1.0×10^{-1} – 8.1×10^{-6} |
| 30 | 23.5 | 1.0×10^{-1} – 5.0×10^{-5} |
| Methanol | | |
| 10 | 28.9 | 1.0×10^{-1} – 4.5×10^{-6} |
| 25 | 28.6 | 1.0×10^{-1} – 9.9×10^{-6} |
| 30 | 20.4 | 1.0×10^{-1} – 3.4×10^{-5} |

Table 3 Selectivity coefficients of the developed Ni(II) sensor using fixed interference method at 1.0×10^{-2} M concentration of interfering ion

| Interfering ion (X) | $K_{Ni^{2+},X}^{pot}$ | Interfering ion (X) | $K_{Ni^{2+},X}^{pot}$ |
|---------------------|-----------------------|---------------------|-----------------------|
| Na ⁺ | 9.2×10^{-2} | Fe ²⁺ | 4.3×10^{-3} |
| K ⁺ | 8.4×10^{-3} | Cu ²⁺ | 3.4×10^{-3} |
| Mg ²⁺ | 3.1×10^{-3} | Zn ²⁺ | 8.7×10^{-3} |
| Ca ²⁺ | 5.5×10^{-3} | Sn ²⁺ | 6.2×10^{-3} |
| Ba ²⁺ | 9.1×10^{-3} | Hg ²⁺ | 6.9×10^{-3} |
| Sr ²⁺ | 3.7×10^{-3} | Pb ²⁺ | 6.7×10^{-3} |
| Cr ³⁺ | 2.8×10^{-3} | Ag ⁺ | 8.9×10^{-3} |
| Mn ²⁺ | 5.4×10^{-3} | Cd ²⁺ | 2.9×10^{-3} |
| Co ²⁺ | 7.6×10^{-3} | | |

Table 4 Determination of the Ni(II) content in real samples

| Sample | Developed Ni(II) sensor, ppm ^a | ICP-AES, ppm |
|------------------|---|--------------|
| Chocolate sample | 0.91 ± 0.02 | 0.92 |
| Vanaspati | 1.07 ± 0.01 | 1.09 |
| Effluent sample | 2.91 ± 0.03 | 2.93 |

a. Average of three replicates.

equilibrium value, was found to 20 s. The potentials generated by the developed sensor remained stable for around 5 min. The sensor was used for a period of 4 months without observing any significant change; but after this period, the slope varied slightly to a lower value.

Effect of pH and non-aqueous media

The pH dependence of the developed Ni(II) sensor was examined for the 1.0×10^{-3} M and 1.0×10^{-4} M solutions over the pH range 2.0 – 9.0. The pH was adjusted by adding drops of 1.0 M HNO₃ or NH₄OH. The results presented as Fig. 3 reveal that the potentials are independent of pH in the range of 3.6 – 7.4 and this range is taken as the working pH range of the Ni(II) sensor. Variation of potentials above and below these pH values can be related to hydrolysis of Ni(II) (at higher pH) and the competition of H⁺ with Ni(II) (at lower pH values).

The working of the sensor in partially non-aqueous media was also investigated using methanol-water and ethanol-water mixtures because real samples, especially industrial effluents, may contain non-aqueous contents. The sensor worked satisfactorily in mixtures having 25% (v/v) non-aqueous content and the results are consolidated in Table 2. Above 25%, the drift in potential may be due to the leaching of the ionophore.

Table 5 Comparison of characteristics of the presently developed sensor with those of some reported sensors

| Sensor | Working concentration range/M | Slope/mV decade of activity ⁻¹ | pH range | Life time/ months | Ref. |
|--------|---|---|-----------------|-------------------|-----------------|
| 1 | $1.0 \times 10^{-1} - 1.0 \times 10^{-3}$ | Non-Nernstian | NM ^a | NM | 7 |
| 2 | $1.0 \times 10^{-1} - 5.0 \times 10^{-5}$ | Non Nernstian | 3.5 - 6.5 | 5 - 6 | 8 |
| 3 | $1.0 \times 10^{-1} - 5.0 \times 10^{-5}$ | Non-Nernstian | 3.5 - 8.0 | NM | 9 |
| 4 | $1.2 \times 10^{-2} - 6.3 \times 10^{-4}$ | Near Nernstian | NM | NM | 10 |
| 5 | $1.0 \times 10^{-1} - 4.0 \times 10^{-5}$ | Nernstian | 3.0 - 7.5 | 2 | 11 |
| 6 | $5.5 \times 10^{-3} - 2.0 \times 10^{-6}$ | Nernstian | 4.0 - 8.0 | 1.5 | 12 |
| 7 | $1.0 \times 10^{-2} - 1.0 \times 10^{-7}$ | Near Nernstian | 4.0 - 7.0 | 3 | 13 |
| 8 | $1.0 \times 10^{-1} - 2.0 \times 10^{-6}$ | Non-Nernstian | 2.0 - 7.0 | 6 | 14 |
| 9 | $1.0 \times 10^{-2} - 5.0 \times 10^{-6}$ | Nernstian | 3.5 - 7.5 | 1 | 15 |
| 10 | $1.0 \times 10^{-1} - 5.0 \times 10^{-6}$ | Nernstian | 3.6 - 7.4 | 4 | Proposed sensor |

a. NM, not mentioned.

Potentiometric selectivity

Selectivity is one the most important characteristic of a sensor. The potentiometric selectivity of the developed Ni(II) sensor was determined using the fixed interference method^{30,31} using the equation $K_{A,B}^{pot} = a_A/(a_B)^{Z_A/Z_B}$. The selectivity coefficients were determined at 1.0×10^{-2} M concentration of foreign ions. The selectivity coefficient values are shown in Table 3; the values indicate that the developed Ni(II) sensor is selective to the Ni(II) ion over a number of cations.

Analytical applications

The developed Ni(II) sensor was successfully applied to the determination of nickel in chocolate (Cadbury's Fruit & Nut), vegetable oil (Dalda) and wastewater sample from electroplating industries. The results are comparable to those obtained by ICP-AES and they are consolidated in Table 4.

The developed Ni(II) sensor was also successfully applied as an indicator electrode in conjunction with Ag/AgCl in the potentiometric titration of Ni(II) solution with EDTA; the titration curve is shown in Fig. 4. The plot is not of sigmoid shape but the sharp break point corresponds to the stoichiometry of the Ni-EDTA complex.

Conclusions

The membrane incorporating a Schiff base containing a binaphthyl moiety as the ionophore has been used for the preparation of a Ni(II) sensor. The developed sensor is very easy to prepare and is found to have good characteristics in terms of slope, concentration range, detection limit, response time, pH range and shelf life. It is also found to be highly selective over a number of cations. A comparison of the characteristics of the presently developed sensor with that of some of the reported sensors is presented as Table 5. An examination of the table reveals that the proposed sensor is superior in terms of working concentration range,^{7-12,14,15} slope,^{7-10,13,14} life time^{7,9,10-12} and pH range.^{7,8,10,13} There are only a few good reports on the application of the reported sensors in environmental or real samples and in this respect the proposed sensor is far superior as it can be used in the determination of Ni(II) in real samples: wastewater from electroplating unit, chocolate sample and hydrogenated vegetable oil sample.

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References

1. E. Bakker, P. Bühlmann, and E. Pretsch, *Chem. Rev.*, **1997**, *97*, 3083.
2. P. Bühlmann, E. Pretsch, and E. Bakker, *Chem. Rev.*, **1988**, *98*, 1593.
3. E. Berman, "Toxic Metals and Their Analysis", **1980**, Heyden & Sons, London, 66.
4. T. P. Coogan, D. M. Latta, E. T. Snow, and M. Costa, *CRC Crit. Rev. Toxicol.*, **1989**, *19*, 341.
5. D. A. Skoog, D. M. West, and F. J. Holler, "Fundamentals of Analytical Chemistry", 7th ed., **1996**, Saunders College Publishing, USA, 75.
6. Z. Marczenko, "Separation and Spectrophotometric Determination of Elements", **1986**, John Wiley & Sons, New York, 393.
7. E. Pungor, K. Toth, and J. Havas, *Acta Chim. Acad. Sci. Hung.*, **1966**, *48*, 17.
8. S. P. Aswathi, V. T. Kulkarni, and M. Sundaresan, *J. Electrochem. Soc. India*, **1988**, *37*, 309.
9. U. S. Lal, M. C. Chattopadhyaya, and A. K. Dey, *J. Ind. Chem. Soc.*, **1982**, *49*, 493.
10. M. D. Hampton, C. A. Peters, and L. A. Wellington, *Anal. Chim. Acta*, **1987**, *194*, 171.
11. G. N. Rao, S. Srivastava, S. K. Srivastava, and M. Singh, *Talanta*, **1996**, *43*, 1821.
12. M. F. Mousavi, N. Alizadeh, M. Shamsipur, and N. Zohari, *Sens. Actuators, B*, **2000**, *66*, 98.
13. M. R. Ganjali, M. Hosseini, M. Salavati-Niasari, T. Poursaberi, M. Shamsipur, M. Javanbakht, and O. R. Hashemi, *Electroanalysis*, **2002**, *14*, 526.
14. L. P. Singh and J. M. Bhatnagar, *Sensors*, **2003**, *3*, 393.
15. K. Belhamel, R. Ludwig, and M. Benamor, *Microchim. Acta*, **2005**, *149*, 145.
16. K. G. Kumar and R. Muthuselvi, *Microchim. Acta*, **2001**, *137*, 25.
17. K. G. Kumar and R. Muthuselvi, *J. Anal. Chem.*, **2006**, *61*, 28.
18. M. Grigoras, C. O. Catanescu, and G. Colotin, *Macromol. Chem. Phys.*, **2001**, *202*, 2262.
19. K. Cammann, "Working with Ion-selective Electrodes", **1979**, Springer-Verlag, Berlin, 82.

20. W. E. Morf, D. Amman, and W. Simon, *Chimia*, **1974**, 28, 65.
 21. P. Bühlmann, S. Yajima, K. Tohda, and Y. Umezawa, *Electrochim. Acta*, **1995**, 40, 3021.
 22. P. Bühlmann, S. Yajima, K. Tohda, K. Umezawa, S. Nishizawa, and Y. Umezawa, *Electroanalysis*, **1995**, 7, 811.
 23. S. Yajima, K. Tohda, P. Bühlmann, and Y. Umezawa, *Anal. Chem.*, **1997**, 69, 1919.
 24. D. Amman, "Ion-selective Microelectrodes: Principles, Design and Application", **1986**, Springer-Verlag, Berlin, 15.
 25. D. Amman, W. E. Morf, P. Anker, P. C. Meier, E. Pretsch, and W. Simon, *Ion-Sel. Electrode Rev.*, **1983**, 5, 3.
 26. P. C. Meier, W. E. Morf, M. Laubli, and W. Simon, *Anal. Chim. Acta*, **1984**, 156, 1.
 27. R. Eugster, P. M. Gehrig, W. E. Morf, U. E. Spichiger, and W. Simon, *Anal. Chem.*, **1991**, 63, 2285.
 28. W. E. Morf, G. Kahr, and W. Simon, *Anal. Lett.*, **1974**, 7, 9.
 29. M. Huser, P. M. Gehrig, W. E. Morf, W. Simon, C. Lindner, J. Jeney, K. Toth, and E. Pungor, *Anal. Chem.*, **1991**, 63, 1380.
 30. E. Bakker, E. Pretsch, and P. Bühlmann, *Anal. Chem.*, **2000**, 72, 1127.
 31. R. P. Buck and E. Lindner, *Pure Appl. Chem.*, **1994**, 66, 2527.
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