Pergamon

Talanta, Vol. 41, No. 2, pp. 301–307, 1994

0039-9140/94 $6.00 + 0.00

DISCONTINUOUS-FLOW POTENTIOMETRIC DETERMINATION OF CHLORIDE IN A LARGE-VOLUME WALL-JET CELL USING AN ION-SELECTIVE ELECTRODE BASED ON A SILVER CHLORIDE FILM CHEMICALLY DEPOSITED ON A SILVER IODIDE SUPPORT

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(*Received* 8 *February* 1993. *Revised* 25 *March* 1993. *Accepted* 10 *August* 1993)

Summary—A robust and sensitive chloride ion-selective electrode can be prepared by modifying the surface of an iodide-selective electrode using the chemical reaction with mercuric chloride in an oxidizing medium containing excess chloride. A thin film of silver chloride is thus formed ensuring a rapid and reproducible response to chloride. The analytical parameters of this electrode are similar to those of commercial silver chloride ion-selective electrodes, but its electrical impedance and signal noise are substantially lower and the response somewhat faster. Its sensitivity toward surfactants is somewhat suppressed. The electrode was used for discontinuous flow potentiometric (DFP) determinations in a large-volume wall-jet cell in which the electrode surface can be continuously reactivated by a cleaning solution contained in the cell. The method was applied to determination of chloride in ground waters from an industrial waste dumping site. The limit of determination is low, 9 μg Cl^-/l ($2.6 \times 10^{-7}M$), the precision good (the relative standard deviation varies from 0.6 to 3.0% for chloride contents from 2.90 to 0.15 mg/l, respectively) and the method correlates satisfactorily with the results of an indirect AAS determination of chloride. The sample throughput is high—90 measurements can be carried out per hour, corresponding to 30–40 determinations per hour.

It has been demonstrated[1] that flow potentiometry with ion-selective electrodes (ISEs) in a large-volume wall-jet cell not only permits highly sensitive and rapid determinations of some ions, *e.g.* fluoride and chloride, but also makes it possible to continuously chemically reactivate the ISE membrane surface, thus ensuring a good long-term reproducibility of the results. The chloride ISEs based on a single crystal and precipitate silver chloride membranes exhibit reasonable selectivity and a sensitivity toward redox agents lower than that of membranes containing mercury ions.[2] On the other hand, they suffer from a higher impedance and membrane passivation by compounds forming insoluble substances with silver ions (*e.g.* various sulphur compounds, cyanide, bromide and iodide). The problem of a high impedance can be alleviated by placing an impedance converter close to the ISE membrane.[3,4] The interferents must be masked or removed; some of them can be removed in flow systems by selective oxidation (*e.g.* bromide, iodide, sulphide and cyanide by oxidation with bromate in nitric acid).[5] Another possibility is continuous regeneration of the membrane with diaminocyclohexanetetraacetic acid (DCTA) in a large-volume wall-jet cell.[1]

The silver/silver chloride electrode was used as early as in 1935 for direct potentiometric determination of chloride[6] and now it has found growing application in flow-injection measurements.[7–10] This electrode, especially in a tubular form,[10] exhibits good analytical properties and the silver chloride film is readily renewed.

A study of the surface properties of silver sulphide,[11] bromide[12] and chloride[13] ISE membranes has shown that high concentrations of interferents, *e.g.* Hg^{2+}, Cl^-, Br^- or I^-, cause substantial changes in the composition of the membranes, leading to changes in the ISE selectivity. This fact offers possibilities for deliberate chemical modifications of ISE surfaces, in order to utilize certain ISEs with a low impedance and stable potential as supports for layers sensitive to ions other than the original ion sensed. For example, solid-membrane ISEs for Ag^+, Cu^{2+} and I^- are promising as these supports.

This work deals with chemical modification of a silver iodide ISE with mercuric chloride, yielding an AgCl-film electrode selective for chloride ions. The analytical parameters of this electrode are favourable and thus the electrode has been applied to direct determination of chloride in ground waters, using discontinuous-flow potentiometric (DFP) measurement in a large-volume wall-jet detection cell.

EXPERIMENTAL

Apparatus

The potentiometric measurements were carried out using an ION-85 instrument and a REC-80 chart recorder with a REA-120 module (all from Radiometer, Copenhagen, Denmark). The test solutions were aspirated by a type 315 peristaltic pump (Zalimp, Warsaw, Poland) from polypropylene beakers and the sample size was controlled by controlling the aspiration time. The sample solutions were fed to the large-volume wall-jet cell described in detail in our previous work.[1] The experimental parameters were the same as in Ref. 1 (the PTFE inlet tubing 1 mm in internal diameter with a 0.3 mm polyethylene jet at a distance of 3–6 mm from the ISE surface, at a flow rate of 2–3 ml/min; the cell contained 50 ml of the reactivation solution and air was pumped between the individual samples stirring the reactivation solution around the ISE).

The commercial chloride and sulphide ISEs, Crytur types 17–27 and 16–27, respectively, were obtained from Monokrystaly, Turnov, Czech Republic. The chloride ISE contained an impedance converter[4] with a WSH-220 operational amplifier (Tesla, Lanškroun, Czech Republic). The saturated silver/silver chloride reference electrode used was the RAE-112 double-junction type (Monokrystaly) with the liquid bridge containing $1M$ potassium nitrate.

Reagents

Analytical grade chemicals were used as received from Lachema, Brno, Czech Republic, Fluka, Buchs, Switzerland (sodium dodecylsulphate) and Serva, Heidelberg, Germany (Triton X-100). The acetate buffer solution employed was $0.5M$ in sodium nitrate, hydroxide and acetate and its pH was 4.6. The $0.1M$ mercuric chloride solution was prepared by dissolving 2.715 g of the substance in 20 ml of $5M$ hydrochloric acid and diluting with water to 100 ml. The reactivation solution was prepared by mixing 10 ml of the above $0.5M$ acetate buffer of pH 4.6 with 39 ml of water and adding 0.5 ml of 30% hydrogen peroxide and 0.05 ml of the above $0.1M$ mercuric chloride solution (*i.e.* the approximation concentrations obtained were $0.1M$ sodium nitrate, hydroxide and acetate, $10^{-4}M$ mercury(II), $1.1 \times 10^{-3}M$ chloride and 0.3% (v/v) hydrogen peroxide). The sample solutions were mixed with the $0.5M$ acetate buffer and diluted with water to obtain the resultant buffer concentration of $0.1M$.

Preparation of the AgCl-film ISE

A Crytur type 53–17 iodide ISE (Monokrystaly) was used as the support. The silver iodide membrane was polished with soft, dry paper tissue; if the membrane was heavily contaminated or scratched, it was first polished with an alumina suspension (1 μm, Struers Scientific Instruments, Denmark). The clean electrode was then immersed for 10 min in a quiescent solution containing $0.01M$ mercuric chloride, 3% (v/v) hydrogen peroxide and $0.1M$ hydrochloric acid. After rinsing with water, the ISE was prepared for use.

Measuring procedure

The distance of the jet from the measuring ISE in the cell was adjusted to 3–6 mm as described in Ref. 1, the cell was filled with 50 ml of the reactivation solution and the cell voltage allowed to stabilize (usually less than 10 sec). The pH of the sample solution was adjusted between 3 and 7 with sodium hydroxide and nitric acid, using methyl orange as the indicator. A volume of up to 4 ml of the sample solution was then measured to a polyethylene test tube, 1 ml of the $0.5M$ acetate buffer of pH 4.6 was added and the volume of the mixture adjusted to 5 ml with water if the sample volume was less than 4 ml. The test tube was stoppered and its contents mixed. The solution was then pumped for 10 sec at a rate of 2–3 ml/min, recording the ISE potential. Air was pumped between the samples.

The apparatus was calibrated by a series of standard chloride solutions in the $0.1M$ acetate buffer at intervals necessary for attaining a required precision, at least before and after a series of *ca* 180 measurements (60–80 samples). The ISE potential decreased with increasing chloride concentration; hence the peak height decreased on injection of samples with increasing chloride contents and the baseline, determined by the reactivation solution containing $1.1 \times 10^{-3}M$ chloride, exhibited the lowest potential (samples with chloride contents higher than that in the reactivation solution produce peaks below the baseline). As the baseline was subject to a greater experimental error and might exhibit a drift, it was preferable to measure the sample peak height relative to the peak corresponding to the standard solution with the highest chloride concentration; possible drift of the ISE potential was also suppressed by frequent measurement of this standard solution. It is recommended to replace the reactivation solution in the cell after *ca* 180–200 measurements.

RESULTS AND DISCUSSION

When the AgI membrane of an iodide ISE is exposed to a solution containing mercuric chloride, then the reaction,

$$2\,AgI(s) + HgCl_2(aq) \rightleftharpoons 2\,AgCl(s) + HgI_2(s) \qquad (1)$$

occurs and the membrane surface is covered by sparingly soluble silver chloride ($pK_s = 9.62–10.4$) and mercuric iodide ($pK_s = 27.95$).[14] If reaction (1) takes place in the presence of excess chloride ions, then the silver chloride formed predominates on the membrane surface because mercuric iodide dissolves in the reaction solution owing to the formation of soluble complex ions of the type $[HgI_2Cl_x]^{x-}$. The electrode thus begins to function as a chloride selective ISE.

Problems may arise due to easy reduction of mercuric iodide to highly insoluble mercurous iodide (pK_S around 28), *e.g.* by impurities present in water. The ISE membrane response to chloride then substantially decreases. To prevent this reaction, an oxidant must be continuously present; we have found hydrogen peroxide to be suitable for the purpose and added it to both the modifying and the reactivating solution.

A reaction analogous to equation (1) occurs when a silver sulphide membrane is modified with a mercuric chloride solution. However, the highly insoluble mercuric sulphide formed (pK_S greater than 50) remains on the membrane surface and causes a greater noise and poorer reproducibility in measurement of the response towards chloride, compared with the modified silver iodide membrane. For this reason, we did not further pursue modification of the sulphide ISE.

The conditions for the preparation and reactivation of the AgCl-film chloride-sensitive ISE was optimized and the electrode was then applied to DFP determination of chloride. All the conditions are described in detail in the Experimental Section. The analytical parameters of the film ISE in this determination were compared with those obtained using a commercial chloride ISE with an AgCl membrane.

Analytical parameters of the AgCl-film ISE

The effects of the solution pH and of redox systems on the ISE signal can be seen in Fig. 1 for the film ISE and a commercial AgCl-ISE. The potential was measured in the absence of chloride, at hydrogen peroxide concentrations of zero and 0.3% (v/v). It is evident that the behaviour of the two electrodes is identical. The pH dependence corresponds to the literature[2,15] and the ISE potential is virtually independent of the pH from *ca* 2.5 up to the highest studied value, *i.e.* 4.6. The presence of hydrogen peroxide does not affect the ISE potential over the whole studied pH range and thus hydrogen peroxide can be used to remove interference of the other halides and sulphide.[16,17]

The selectivity coefficients for the principal interferents (*i.e.* the other halides, cyanide, sulphide) are virtually identical for the film and commercial ISEs. The time constants of the film

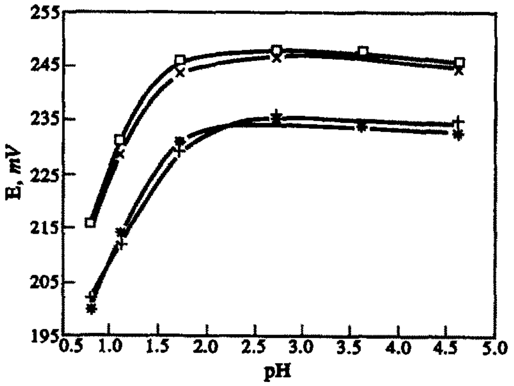

Fig. 1. The effect of the pH and a redox system on the potentials of the film and commercial chloride-sensitive ISEs. Commercial ISE: + in the absence of 0.3% (v/v) H_2O_2 and * in its presence. Film ISE: ☐ in the absence of 0.3% (v/v) H_2O_2 and x in its presence. For the conditions of the DFP measurement see the Experimental Section.

Table 1. The time constants of the film and commercial ISEs (the conditions as in the other measurements, flow rate, 4 ml/min). T_k is the time required to attain 63.2% of the maximum response on a step change in the analyte concentration

	T_k (*sec*)	
$p\text{Cl}^-$	Commercial ISE	Film ISE
6.4	1.3	0.8
4.7	1.0	0.6
3.7	0.8	0.4

ISE are smaller than those of a commercial ISE (Table 1; cf. also Table 1 in Ref. 1). Moreover, these values are the same even in the presence of serious interferents (*e.g.* cyanide or sulphide at a concentration of $2 \times 10^{-5} M$) while the commercial electrode behaviour becomes erratic.

Figure 2 depicts the calibration dependence for the film ISE. It can be seen that at low chloride concentrations, for $p\text{Cl}^- > 4.1$, the slope of the dependence gradually decreases below 53 mV per concentration decade and at $p\text{Cl}^- > 4.7$ the potential becomes a linear function of the chloride concentration, with a correlation coefficient of 0.9991. The whole calibration dependence can be fitted with a higher-order polynomial which is then readily applicable to series determinations. The noise of the potential values is very low (less than 0.1 mV) and thus the limit of determination, defined as three times the standard deviation of the noise,[18] is also low and amounts to 9 μg/l ($2.6 \times 10^{-7} M$). The reproducibility of the absolute potential values on recalibration is excellent, indicating highly efficient reactivation of the electrode surface.

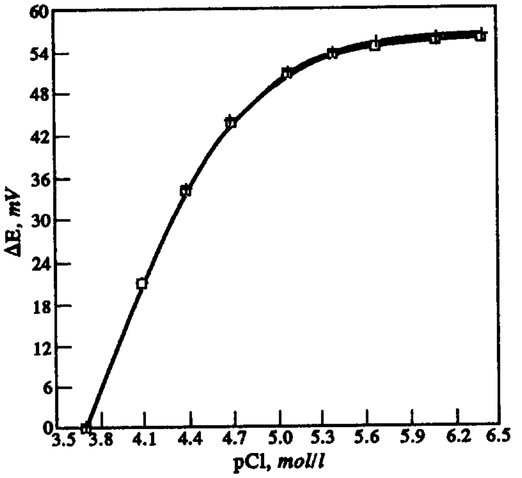

Fig. 2. The calibration plots for the film ISE. For the conditions of the DFP measurement see the Experimental Section. (ΔE is the difference between the actual potential and the potential corresponding to the highest chloride concentration.)

The response of the film ISE was not significantly influenced by gradual diluting of the reactivation solution in the cell during 180 measurements carried out within 2 hr; the only effect is a gradual increase in the baseline potential caused by decreasing concentration of chloride on dilution. Therefore, it is recommended to replace this solution after 180–200 measurements.

In application of ISEs, a frequent problem is passivation by surface active substances. Therefore, the effect of a cationic, anionic and a nonionic surfactant was studied at three chloride concentrations ($p\text{Cl}^-$ of >6.4, 4.7 and 3.7) and two surfactant concentrations (2 and 20 mg/l). The model surfactants were Hyamin (cationic), sodium *n*-dodecylsulphate (anionic) and Triton X-100 (nonionic). The measurements were carried out both with the film and the commercial ISE. The reactivation solution in the cell was the same for both the electrodes (see Experimental), only mercuric chloride was absent with the commercial ISE.

The results can be seen in Figs 3(A) and (B), indicating that the film ISE is substantially more resistant towards all types of surfactant at higher chloride concentrations. At low chloride contents, the effects of the anionic surfactant are similar on the two electrodes, while the cationic surfactant affects somewhat more the potential of the film ISE. The effect of the nonionic surfactant is generally small. The presence of the surfactants, primarily the cationic one, causes potential drift and a decrease in the response rate with both the electrodes. However, the film ISE exhibits a smaller noise in the presence of surfactants than the commercial ISE.

The influence of another important factor in flow analyses of real samples, solution viscosity, was studied at two chloride concentration levels ($p\text{Cl}^{-1} = 6.1$ and 5.1) with the film ISE at 25°C in the presence of glycerol in the sample solution, over a dynamic viscosity range of 1.2–4.1 Pa.s (12.3 to 45.7% (v/v) of glycerol). Glycerol was not present in the reactivation solution. It can be seen from Fig. 4 that the slope of the potential *vs* concentration dependence is not much affected, but that the absolute potential values decrease considerably. These effects can be minimized by matching the viscosities of the samples and the calibration solutions.

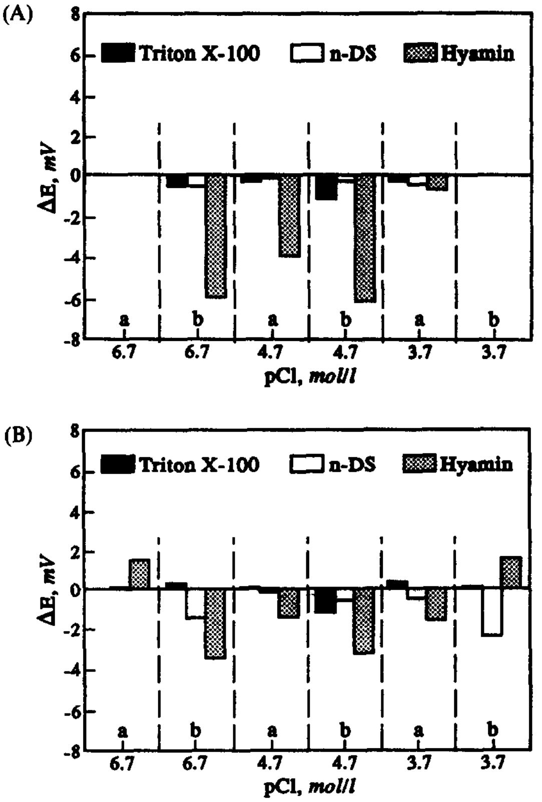

Fig. 3. The effect of surfactants on the potential of the film ISE (A) and commercial ISE (B). For the conditions of the DFP measurement see the Experimental Section. (ΔE is the difference in the electrode potential in the absence of surfactant and in the presence of (a) 2 and (b) 20 mg/l of surfactant.)

Ground water analysis

The DFP technique with the film ISE was applied to determination of chloride in ground waters with high concentrations of iron, which thus cannot be analyzed by the common visual titration. The results were compared with the values obtained by an independent method based on the precipitation of chloride by excess silver nitrate and determination of the silver excess by atomic absorption spectrometry.[19]

The analyses of 22 samples of ground waters from the Sulkov area, where wastes from the Škoda Works are dumped, gave chloride concentrations from 6.2 to 169 mg/l. The correlation between the results obtained by DFP and AAS,

$$y_{\mathrm{AAS}} = a + s_{\mathrm{a}} t_{\alpha} + (b + s_{\mathrm{b}} t_{\alpha}) x_{\mathrm{DFP}}$$

for significance level $\alpha = 0.05$, is very good and is given by

$$y_{\mathrm{AAS}} = 3.6 \pm 1.5 + (1.027 \pm 0.029) x_{\mathrm{DFP}}$$

with a correlation coefficient of 0.9982 (Fig. 5). The value of $a = 3.6 \pm 1.5$ is significantly different from zero and indicates a constant systematic error caused probably by a side interaction of silver ions in the AAS determination (*e.g.* adsorption of Ag^+ on the walls of the centrifuge test tubes). However, this error is not very large and represents a maximum chloride concentration of 5.1 mg/l. The value of $b = 1.027 \pm 0.029$ is not significantly different from unity and thus the results are subject to no proportional systematic error.

The precision of measurement is very good: The relative standard deviations, calculated from five parallel determinations, equal 3.0, 0.8 and 0.6% for chloride concentrations of 0.15, 0.70 and 2.90 mg/l, respectively.

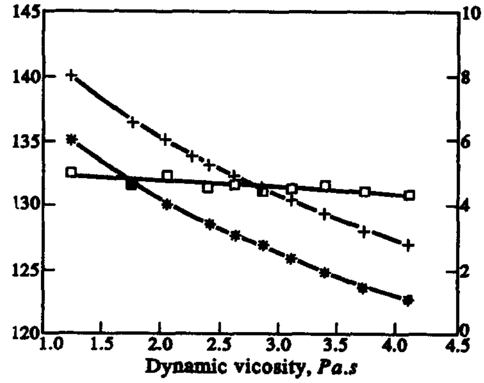

Fig. 4. The effect of the test solution viscosity on the potential of the film ISE and the slope of its response. For the conditions see the text. $+ p\mathrm{Cl}^- = 6.1$; $^* p\mathrm{Cl}^- = 5.1$; □ slope (the difference in the ISE potentials for $p\mathrm{Cl}^{-1} = 6.1$ and 5.1).

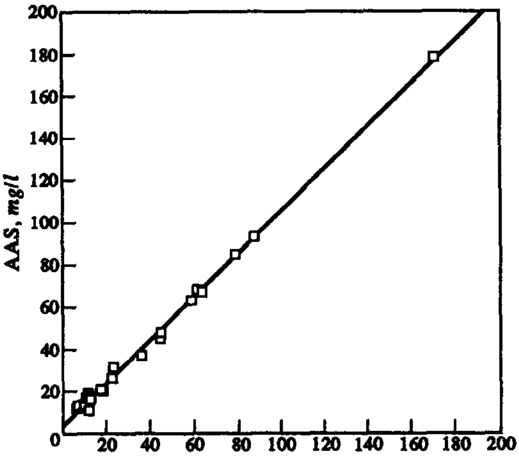

Fig. 5. Correlation of the DFP determination of chloride in ground water with the indirect AAS determination.

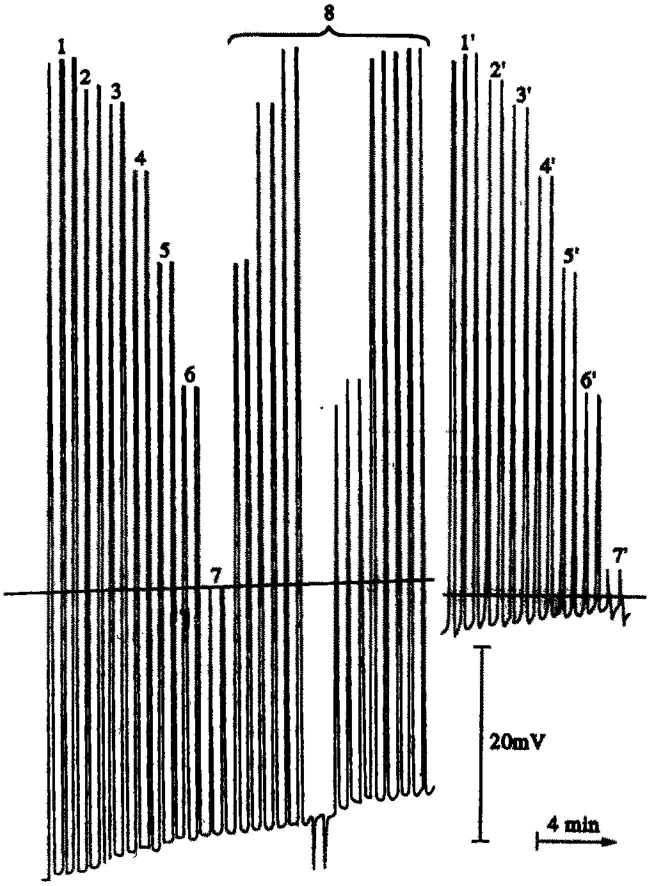

Fig. 6. A recording of the DFP chloride determination. 1–7: calibration prior to determination; 8: samples; 1′–7′: calibration after determination; 1, 1′—blank; 2,2′—0.142; 3,3′—0.284; 4,4′—0.710; 5,5′—1.418; 6,6′—2.840; 7,7′—7.100 mg Cl^-/l.

The chief advantages of the DFP method over AAS is substantially greater sensitivity (the limit of determination is two orders of magnitude lower) and the possibility to determine chloride over a wide concentration range, without the necessity to dilute samples with high chloride concentrations. The DFP method permits 90 measurements per hour, *i.e.* 30–40 samples can be analyzed per hour. An example of a recording is given in Fig. 6. It can be seen that the baseline drifts due to gradual dilution of the reactivation solution, as pointed out in the Experimental Section. Nevertheless, all the measurements can be related to the calibration solution with the highest chloride concentration (samples 7, 7′) samples with higher chloride contents yielding lower peaks than that corresponding to samples 7, 7′, possibly even below the baseline. The apparent break in the baseline before calibration run 1′-7′ is caused by the fact that more samples were analyzed prior to recalibration than those shown in the figure.

CONCLUSIONS

The main advantages of DFP with a film chloride-sensitive ISE can be summarized as follows. An excellent reproducibility of the absolute potential values indicating that the reactivation procedure in the wall-jet cell is very efficient. The film electrode has a low impedance compared with the commercial chloride ISEs, a very low potential noise (less than 0.1 mV) and a somewhat better resistance toward passivation by surfactants. The method is rugged and thus is suitable for samples with complex matrices (*e.g.* soil extracts). The ISE response is rapid and thus the method exhibits a high sample throughput. The advantages of the film ISE are most marked in highly complex samples where the measuring reliability is superior to commercial electrodes. The commercial electrodes may be irreversibly poisoned by cyanide and sulphide, while the film ISE is reactivated during the procedure.

The properties of the film ISE are in some respects similar to the tubular silver/silver chloride electrode.[10] The favourable properties of these two electrodes, primarily the fast response, good reproducibility and sensitivity of measurement, are due to the very thin layer of the ion-sensitive material (AgCl), so that the transport of the analyte to the membrane active sites is fast and reproducible. The two electrodes share a disadvantage—the necessity of preparing the AgCl film prior to a series of measurement, but this procedure is simple. In the case of the chemically produced electrode there are additional advantages in that the preparation procedure is shorter (10 min *vs* 1 hr with the silver/silver chloride electrode) and that the ISE is continuously reactivated during the measurement.

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