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A Mini Review on Silver(I)-Selective Potentiometric Electrodes and Its Applications

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ABSTRACT: Ion-selective electrodes (ISEs) are preferred by analytical chemist in the determination of various ions in routine laboratory analysis. Potentiometric ion-selective electrodes have great advantages and different properties. Silver is an important element due to its wide use in the industry. The widespread use of silver in every field makes its determination important. Today, some analytical methods have been proposed for the determination of silver(I) ions in various samples. However, potentiometric methods have an important place in silver determination due to their versatile advantages. In this mini review, silver(I)-selective electrodes in the literature and their properties were investigated.

Keywords − *Silver(I), potentiometric methods, ion-selective electrode, sensor*

1. Introduction

Silver has wide commercial importance in photographic industry, jewellery, alloys, dental and medical products, optics, electrical and electronic equipment and high capacity silver–based batteries (Purcell and Peters, 1998; Mijnendonckx et al., 2013; Malinowska et al., 1994). Because of its widespread use, silver can cause pollution in the environment, especially in water resources. Silver is nontoxic, but silver absorption can cause liver and kidney disease (Sejmanovic et al., 2011). In addition, silver compounds are often used to purify swimming pools and drinking water due to their bacteriostatic properties (Karimi et al., 2011). Therefore, the determination of silver ions in various environmental, industrial and water samples is extremely important.

Potentiometric ion-selective electrodes were first described by Cremer (1906) and are widely used in different ion analyses. The potentiometric measuring system is based on measuring the potential difference between the reference and working electrode (Özbek et al., 2020). Potentiometry ion-selective electrodes offer great advantages such as wide linear working range, low detection limit, low-energy consumption, short response time, high selectivity and sensitivity, diverse laboratory applications and low cost compared to the other analytical methods such as inductively coupled plasma mass spectrometry (ICP-MS), high-performance liquid chromatography (HPLC), atomic absorption spectrometry (AAS), atomic fluorescence spectrometry (AFS), gas chromatography (GC), X-ray diffraction (XRD) and mass spectrometry (MS) (Isildak et al., 2020a; Topcu et al., 2018; Soleimani and Afshar, 2013; Liang et al., 2009; Özbek et al., 2020). In this review, we aim to provide an overview of the current advances in the silver(I)-selective potentiometric electrodes and its applications.

2. Silver(I)-Selective Potentiometric Electrodes

The components of ion-selective electrodes usually consist of different proportions of poly (vinyl chloride) (PVC) or different a polymer, ionophore, lipophilic salt and plasticizer. These mixtures are commonly referred to as PVC membrane sensors. Ionophore, the most important component of potentiometric ion-selective electrode is responsible for the selective response to the target ion (Isildak et al., 2020b). Molecules containing elements such as nitrogen, oxygen and sulfur in their structure are highly functional and used in many areas (Özbek et al., 2017). In addition, these molecules are preferred by researchers as sensor materials (Isildak et al., 2020a). Calixarene derivative molecules are generally preferred as ionophores in silver(I)-selective electrodes. However, it has been used as ionophore in porphyrin derivatives and similar macrocyclic molecules (Fig. 1). Lipophilic salt (NaTPB or KTpClPB) without ion exchange properties are added to the membrane mixture to increase selectivity. Plasticizers (DEHA, BEHS, NPOE, DBP and DOP etc.) fix the dielectric constant of the membrane (Mihali and Vaum, 2012). The membrane components of silver(I)-selective electrodes in the literature are given in Table 1.

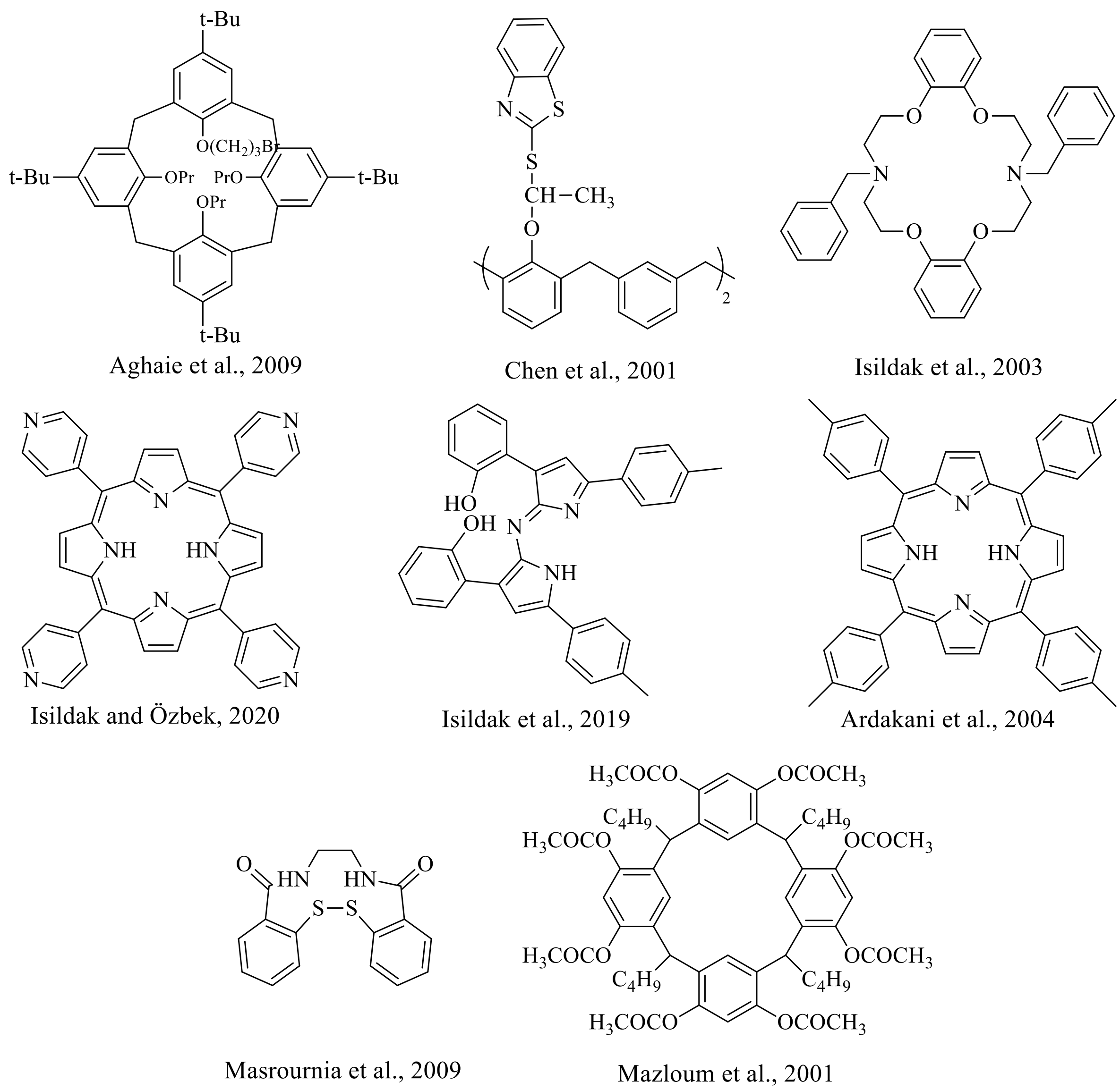

Fig. 1. Chemical structure of some ionophores used in the silver(I)-selective electrodes

Table 1. Membrane components of silver(I)-selective electrodes

Reference	Membrane Composition (*w/w*, %)
Sejmanovic et al. 2011	PVC (44.3); DBP (55.2); NaTPB (0.5)
Isildak and Özbek, 2020	PVC (35.9); BEHS (59.6); KTpClPB (1.0); ionophore (3.5)
Isildak et al., 2019	PVC (34.8); BEHS (61.7); NaTPB (1.0); ionophore (2.5)
Aghaie et al., 2009	PVC (30.0); DBP (62.0); NaTPB (3.0); ionophore (5.0)
Chen et al., 2001	PVC (33.0); NPOE (66.0); ionophore (1.0)
Isildak et al., 2003	PVC (28.0); NPOE (68.0); NaTPB (0.8); ionophore (3.2)
Demirel et al., 2006	PVC (31.5); NPPE (66.0); KTpClPB (0.50); ionophore (1.0)
Ardakani et al., 2004	PVC (20.0); DBP (70.0); NaTPB (4.0); ionophore (6.0)
Mahajan et al., 2001	PVC (32.0); BEHS (66.5); ionophore (1.5)
Masrournia et al., 2009	PVC (33.0); DOP (63.0); ionophore (4.0)
Mazloum et al., 2001	PVC (33.0); DBP (57.0); NaTPB (6.0); ionophore (4.0)
Mahajan et al.,2002	PVC (31.5); BEHS (66.7); ionophore (1.8)

2.1. Working concentration range, detection limit and slope value of silver(I)-selective electrodes

Working concentration range is one of the most important features of ion-selective electrodes and and defines the concentration range in which a sensor can operate linearly. Limit of detection (LOD) of ion-selective electrodes is defined as the lowest ion concentration that produces a measurable potential difference in the membrane interface. The detection limit is usully calculated by writing the potential value corresponding to the point where the extrapolations of the two linear regions on the calibration graph intersect, by substituting them in the correct equation (Isildak et al., 2020b). The working concentration range, detection limit and slope values of silver(I)-selective electrodes in the literature are given in Table 2. As seen, the widest working concentration range and the lowest detection limit value belongs to the electrode developed by Ardakani et al. (2004).

Table 2. The working concentration range, detection limit and slope values of silver(I)-selective electrodes

Reference	Concentration range (mol L^{-1})	Limit of detection (mol L^{-1})	Slope (mV/decade)
Sejmanovic et al. 2011	$1.0 \times 10^{-5} – 1.0 \times 10^{-1}$	4.25×10^{-6}	60.25
Isildak and Özbek, 2020	$1.0 \times 10^{-6} – 1.0 \times 10^{-1}$	1.9×10^{-6}	Not reported
Isildak et al., 2019	$1.0 \times 10^{-5} – 1.0 \times 10^{-1}$	7.3×10^{-7}	Not reported
Aghaie et al., 2009	$4.2 \times 10^{-6} – 1.0 \times 10^{-1}$	3.0×10^{-6}	60
Chen et al., 2001	$5.0 \times 10^{-6} – 1.0 \times 10^{-1}$	1.3×10^{-6}	50.6
Isildak et al., 2003	$7.0 \times 10^{-6} – 1.0 \times 10^{-1}$	3.0×10^{-6}	75.0 ± 10.0
Demirel et al., 2006	$1.0 \times 10^{-6} – 1.0 \times 10^{-2}$	8.0×10^{-7}	53.8 ± 1.6
Ardakani et al., 2004	$1.0 \times 10^{-7} – 1.0 \times 10^{-1}$	1.0×10^{-7}	59.2 ± 1.0
Mahajan et al., 2001	$1.0 \times 10^{-5} – 1.0 \times 10^{-1}$	3.0×10^{-6}	59.7
Masrournia et al., 2009	$1.0 \times 10^{-5} – 1.0 \times 10^{-1}$	6.8×10^{-6}	59.8 ± 0.2
Mazloum et al., 2001	$1.0 \times 10^{-5} – 1.0 \times 10^{-1}$	3.0×10^{-6}	58.0 ± 1.0
Mahajan et al.,2002	$1.0 \times 10^{-5} – 1.0 \times 10^{-2}$	5.75×10^{-6}	56.7

2.2. pH working range of silver(I)-selective electrodes

While measuring the pH working range of the ion-selective electrodes, pH 2.0 – 12.0 buffer solutions (Solutions are generally prepared with HNO_3, HCl and NaOH) are prepared and, the range in which no potentially significant change occurs is the pH operating range of the ion-selective electrode. The pH working ranges of silver(I)-selective electrodes are shown in Table 3. As seen, silver(I)-selective electrode working in the widest pH range was proposed by Isildak et al. (2019).

2.3. Response time and life time of silver(I)-selective electrodes

Response time in the ion-selective electrodes is an important physical property and it has been defined by IUPAC as the time taken for 95% of the observed potential change in equilibrium states to occur (Buck and Lindner, 1994). The response time of silver(I)-selective electrodes are given in Table 3. As seen, the response time of the electrodes varies approximately between 3 and 30 seconds. Life time in ion-selective electrode is determined by examining the potential differences they exhibit at certain intervals such as, day, week and month, during the ten-fold concentration change. The life time of silver(I)-selective electrodes are given in Table 3.

Table 3. The pH working range, response time and life time of silver(I)-selective electrodes

Reference	pH working range	Response time (s)	Life time (month)
Sejmanovic et al. 2011	0.7 – 7.0	5 – 30	2
Isildak and Özbek, 2020	4.0 – 10.0	8	Not reported
Isildak et al., 2019	2.0 – 11.0	3	Not reported
Aghaie et al., 2009	4.0 – 8.0	< 15	3
Chen et al., 2001	2.5 – 7.0	< 12	1
Isildak et al., 2003	4.0 – 7.0	< 10	Not reported
Demirel et al., 2006	2.0 – 6.0	5 – 10	2
Ardakani et al., 2004	3.0 – 9.0	< 10	1
Mahajan et al., 2001	1.0 – 5.6	20	6
Masrournia et al., 2009	5.1 – 7.2	~20	2.5
Mazloum et al., 2001	1.5 – 6.0	< 20	2
Mahajan et al.,2002	3.5 – 7.0	< 10	Not reported

2.4. Water samples and other real samples applications of silver(I)-selective electrodes

The most important feature of the newly proposed ion-selective electrodes is their applicability in real samples. Potentiometric ion-selective electrodes are highly successful in real sample analysis and offer high recovery. The real sample applications and recovery of silver(I)-selective electrodes suggested in the literature are given in Table 4. As seen, the proposed silver(I)-selective electrodes have shown very high recoveries in different real sample analyses. When the literature is examined, it is noteworthy that silver(I)-electrodes are mostly used in different water samples. In addition, there is an application on photography, which is one of the other uses of silver (Aghaie et al., 2009) (Table 4).

Table 4. Real sample applications of proposed silver(I)-selective electrodes

Reference	Real Sample	% Recovery
Sejmanovic et al. 2011	Natural mineral water	95.05
	Tap water	100.80
	River water	101.13
	Colloidal silver water	Not reported
Isildak and Özbek, 2020	Precipitated rain water	89.99
	Commercial water	95.00
Isildak et al., 2019	River water	95.63
	Urban water	82.30
	Bottle water	95.0
	Spring water	90.0
Aghaie et al., 2009	Photographic emulsion and photographic films	Not reported
Ardakani et al., 2004	Fixation solutions	Not reported
Mahajan et al., 2001	Water sample spiked	Not reported
Masrournia et al., 2009	Waste water samples	Not reported

3. Conclusion

In this mini-review, potentiometric ion-selective electrodes with silver(I)-selective developed for the determination of silver ions were investigated. Potentiometric properties of these electrodes such as, concentration range, detection limit, slope value, response time, life time and pH working range were compared. Successful results were recorded in some proposed silver(I)-selective electrodes, and applications in real samples (Table 4). As a result, developed silver(I)-selective electrodes can be used routinely for silver ion analysis in various samples due to their different advantages.

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