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Alexandre Sala, Hugues Brisset, André Margaillan, Jean-Ulrich Mullet, Catherine Branger. Electrochemical sensors modified with ion-imprinted polymers for metal ion detection. Trends in Analytical Chemistry, 2022, 148, pp.116536. 10.1016/j.trac.2022.116536 . hal-03606487

HAL Id: hal-03606487

<https://hal.science/hal-03606487>

Submitted on 22 Jul 2024

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Electrochemical sensors modified with ion-imprinted polymers for metal ion detection

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Abstract

Quantification of trace levels of metal ions is an important issue in terms of health and environment safety. Ion-imprinted polymers (IIPs) are synthetic materials that present excellent selectivity properties. Therefore, when combined with electrochemical sensors, proven to be low-cost and time-efficient, they can act as remarkably selective receptors. The development of these type of electrochemical sensors has seen an increase in attention in the past decade. The aim of this review is to give the current state of the art in the conception and performances of IIP-based electrochemical sensors (IIPECS). It is illustrated by many examples of applications that prove the high potential of IIPECS to quantify metal ions in a wide range of real samples with high sensitivity and selectivity.

Keywords

Ion-imprinted polymers; Electrochemical sensors; Potentiometry; Ion-selective electrodes (ISE); Membrane electrodes; Voltammetry; Carbon paste electrodes (CPE); Electropolymerization

Abbreviations and acronyms

3-MPTMS	(3-mercaptopropyl)trimethoxysilane	M.O.	mineral oil
4-VP	4-vinyl pyridine	MBA	N,N'-methylenebis(acrylamide)
AAPTS	[3-(2-aminoethylamino)propyl]trimethoxysilane	MBT	mercaptobenzothiazole
AAPTS	3-(2-aminoethyl-amino)propylmethoxysilane	MIP	molecularly imprinted polymer
AAS	atomic absorption spectroscopy	MNP	magnetic nano-particles
Ag NP	silver nanoparticles	MPM	matched potential method
APTMS	(3-aminopropyl)trimethoxysilane	MWCNT	multi-walled carbon nano tubes
CNT	carbon nano tubes	NAA	neutron activation analysis
CPE	carbon paste electrode	NaTPB	sodium tetraphenylborate
CV AAS	cold vapour atomic absorption spectroscopy	NIP	non-imprinted polymer
DBP	dibutylphthalate	NIPECS	nip-modified electrochemical sensors
DNP	dinonylphthalate	NPOE	2-nitrophenyloctyl ether
DPASV	differential pulse anodic stripping voltammetry	OMNiIP	one monomer ion-imprinted polymer
DPV	differential pulse voltammetry	ORMOSIL	organically modified silicate
DVB	divinylbenzene	P.O.	paraffin oil
EDTA	ethylenediaminetetraacetic acid	PAN	1-(2-pyridylazo)-2-naphthol
EGDMA	ethylene glycol dimethacrylate	PAR	4-(2-pyridylazo)resorcinol
FRP	free radical polymerization	PPy	polypyrrole
GCE	glassy carbon electrode	PVC	polyvinyl chloride
GF-AAS	graphite furnace atomic absorption spectroscopy	RGO	reduced graphene oxide
GNS	graphene nano-sheet	S.O.	silicon oil
I.L.	ionic liquid	SAM	self-assembled monolayer
ICP-AES	inductively coupled plasma atomic emission spectroscopy	SSM	separate solution method
ICP-MS	inductively coupled plasma mass spectrometry	SWASV	square-wave anodic stripping voltammetry
ICTMS	3-isocyanatopropyl trimethoxysilane	SWCNT	single-walled carbon nano tubes
IIP	ion-imprinted polymer	TEOS	tetraethyl orthosilicate
IPECS	IIP-modified electrochemical sensors	TMOS	tetramethyl orthosilicate
ISE	ion-selective electrode	TMSPM	(trimethoxysilyl)propyl methacrylate
KTpCIPB	potassium tetrakis(4-chloro-phenyl) borate	TRIM	trimethylolpropane trimethacrylate
LOD	limit of detection		

1. Introduction

Monitoring of metal ions is a particularly important topic as they can have a negative impact on both the environment and human health [1,2]. Even trace amounts of some metal ions can lead to disastrous consequences so it is essential to develop analysis methods that can reach low detection limits and be efficient even in the case of complex matrices. Though conventional techniques, such as Atomic Absorption Spectroscopy (AAS) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS), have great accuracy and widespread applications for the measurement of the total amount of metals, they suffer from expensive equipment and time-consuming preparation and analysis processes. Thus, in order to easily and quickly monitor the levels of trace metal ions, the development of affordable sensors has become a hot research topic.

Biomimetic electrochemical sensors based on the molecular imprinting technology have already proved their high efficiency for the quantification of organic pollutants [3–6]. In such a case, Molecularly Imprinted Polymers (MIPs) act as efficient and highly selective receptors that will considerably improve the sensitivity of the associated electrodes [7,8]. The development of Ion-Imprinted Polymers (IIPs) for the selective extraction of ion species came after MIPs [9–11]. The growing interest in the preparation of specific electrodes incorporating IIPs for the quantification of metal ions is also more recent [12–15].

Like MIPs for organic targets, IIPs are specially designed to selectively recognize a target ion, called template ion, which is used for their synthesis. The general procedure to prepare IIPs is based on the initial formation of a complex between the template ion and a molecule bearing at least one chelating group, the ligand. The structure of the so-formed complex is then frozen by crosslinking in order to form a 'rigid' three-dimensional network around the complex that will maintain the shape and size of the binding cavities after the template removal (Fig. 1). The properties of selective recognition of IIPs first lead to their use as sorbents for solid-phase extraction [16]. This is still a large area of applications of IIPs that encompasses preconcentration, speciation and removal of metal ions [17–20]. Similarly to MIPs, the selectivity of IIPs makes them particularly interesting as receptors for sensing applications. For optical sensors, this is not straightforward because most metal ions cannot be directly quantified by the measurement of an optical signal. Thus the design of such sensors based on IIPs requires the incorporation of a chromophore [21,22] or a fluoroionophore [23–25] inside the polymer matrix to generate or quench an optical signal (absorbance or fluorescence). Another option is to use fluorescent particles like quantum dots [26–29]. On the other hand, most metal ions can be quantified by electrochemical detection methods, such as voltammetry or potentiometry [30–33]. Therefore, no specific requirements are needed for the conception of IIPs for electrochemical sensors, in which they will act as selective receptors for the binding of the target ion to improve the sensitivity and selectivity. This is of particular interest for applications in various complex samples such as environmental or waste waters, human biological fluids or solid samples in which the analytical difficulties can come from the presence of interfering ions or from the complexity of the matrix. Moreover, coupling the ion-imprinting technology with electrochemical detection can provide IIP-modified electrochemical sensors (IIPECS) which are relatively inexpensive to develop, as a general feature of the IIP preparation. This review aims to provide insight into how IIPs can be used in electrochemical sensors to improve their performances and to show how effective they can be regarding selectivity. In particular, one of the objectives of the present survey is to help scientists in their conception of IIPECS by giving general indications on the design of suitable IIPs and electrodes. For that purpose, the different routes that can be implemented to prepare IIPs are detailed before developing the various strategies to prepare

IIP-modified electrodes for potentiometric and voltammetric applications. A focus on the IPECS characterization and applications is also included.

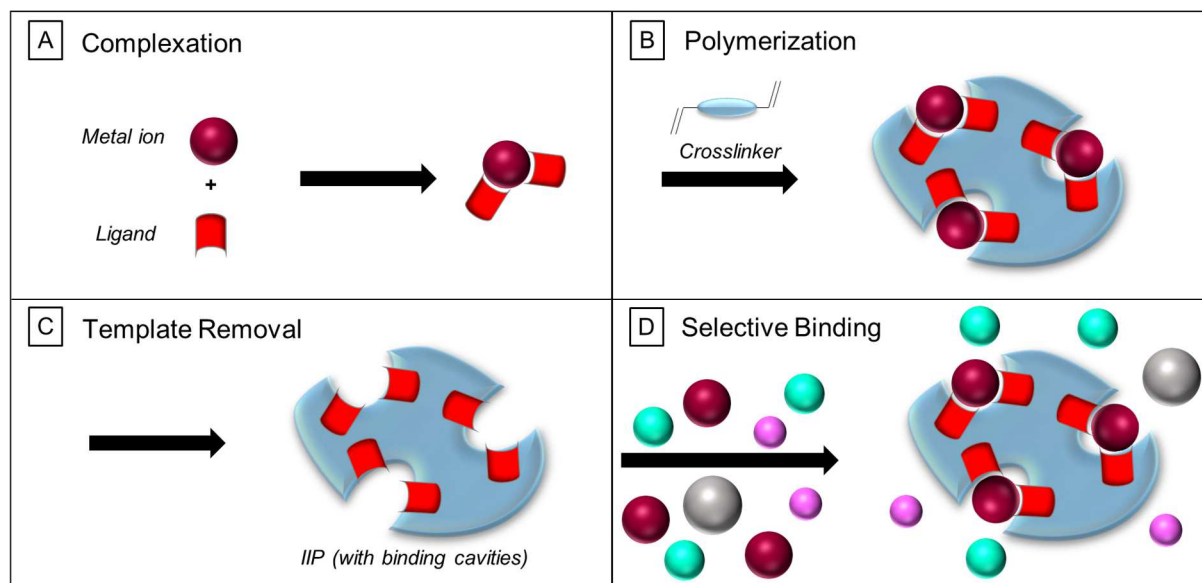


Fig.1. Schematic representation of the synthesis of an Ion-Imprinted Polymer (IIP). A. Coordination complex formed between the target ion and a ligand ; B. Crosslinking to form the polymer containing the coordination complex ; C. Removal of the template to obtain binding cavities ; D. Selective binding of the target ion in the presence of interfering ions

2. Different routes for IIP preparation towards electrochemical sensor design

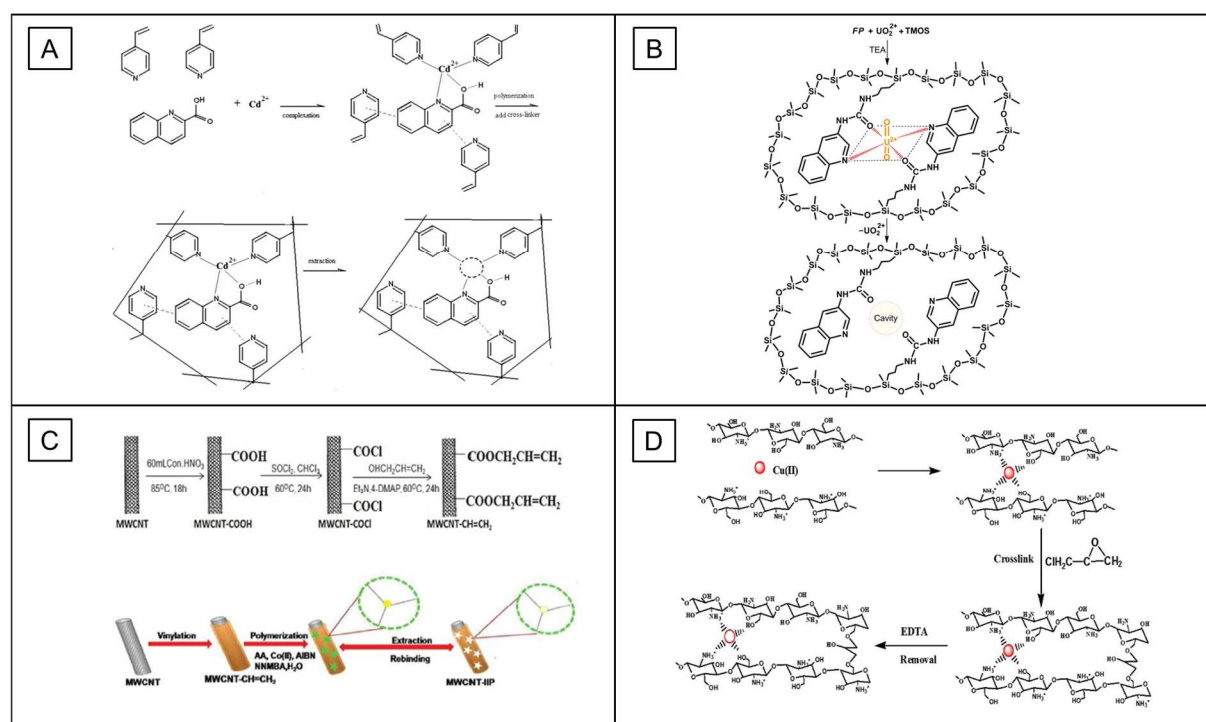


Fig. 2. Different routes of IIP polymerization. A. Free-radical polymerization (Reprinted with permission from Elsevier, Copyright 2011 [12]); B. Sol-gel (Reprinted with permission from Elsevier, Copyright 2016 [34]); C. Surface imprinting of nano-particles (Reprinted with permission from Taylor & Francis, Copyright 2018 [35]); D. Crosslinking of linear chains (Reprinted with permission from Elsevier, Copyright 2019 [36]).

2.1. Free radical polymerization

Free Radical Polymerization (FRP) is the most common method to synthesize IIPs as the process is well-established and easy to implement [37,38]. FRP involves the use of vinylated monomers. For that purpose, commercial vinylated crosslinkers such as ethylene glycol dimethacrylate (EGDMA), divinylbenzene (DVB), N,N'-methylenebis(acrylamide) (MBA), or trimethylolpropane trimethacrylate (TRIM) are generally employed.

The formation of the selective binding cavities of imprinted polymers is a crucial step to ensure their high recognition properties. In the case of IIPs, a coordination complex must be formed with the template ion before the crosslinking step. This requires the use of a ligand or a functional monomer bearing some chelating groups (Fig.2.A). In this first case, the ligand is not covalently-bound to the three-dimensional polymer network but is simply trapped thanks to non-covalent interactions with either the crosslinker [39] or with an additional monomer [9] such as acrylic acid, methacrylic acid, or 4-vinylpyridine (4-VP) [40,41]. Most of the time, commercial ligands are used, such as dithizone [39,42], 1-(2-pyridylazo)-2-naphthol (PAN) [43–45] or 4-(2-pyridylazo)resorcinol (PAR) [46], for instance. But, to improve the selectivity thanks to a more specific ligand, a few authors choose to

synthesize it: aza-thioether crown [40] and 1,2-bis(quinolin-8-ylsulfanylmethyl)benzene [47] for Ag(I) or 5,10,15,20-tetrakis(3-hydroxyphenyl)-porphyrin for Hg(II) [48].

Although this “trapping” procedure is widely used for IIP synthesis because of its easy implementation, it presents a major drawback: there is a huge risk that the ligand can be leached out of the polymer matrix during the removal of the template ion as demonstrated by Moussa et al. [49]. While some authors compare infrared spectra before and after leaching to show that the ligand remains trapped in the network, Shamsipur et al. state that the amount of ligand is too insignificant when compared to other components of the polymer, making it impossible to confirm or not the presence of ligand by infrared spectroscopy [40]. In their preparation of IIP particles for Hg(II) detection, Velepini et al. worked on an original system where the trapped ligand is a high molecular weight crosslinked carboxymethyl cellulose modified by thiol groups. Due to its size, this ligand should thus be further retained inside the polymer network [50].

A more straightforward way to prevent ligand-leaching is to incorporate it via covalent bonding in the polymer matrix. In this case, the ligand must contain functionalities that can be polymerized. Thus, the ligand in the form of a functional monomer will not be leached out of the IIP during removal of the target or during use. Some functional monomers are commercially available, as, for example, itaconic acid for Hg(II)-imprinted polymers [51–53]. While in other cases, when more specific chelating groups are desired, they must be synthesized: this can, for example, be easily achieved by reacting an amine-bearing ligand with acrylic or methacrylic acid or methacryloyl chloride to form an amide functional monomer [54,55]. Prasad et al. employed a more original strategy by preparing One MoNomer Ion Imprinted Polymer (OMNiIP) in which a single crosslinking monomer acts as both the functional chelating monomer and the crosslinker. For this, they mixed an algae (*Aulosira sp.*) with acryloyl chloride to form a multi-acryloylated algae that can readily be used as a crosslinking functional monomer to make OMNiIP films for the electrochemical sensing of Cu(II) [56].

2.2. Sol-gel

Sol-gel technology has recently been explored for the design of molecularly imprinted materials especially for their use in electrochemical and optical sensors [57]. They are usually hybrid organic-inorganic materials of the ORMOSIL (Organically MODified SILicate) class (Fig. 2.B). As such, they are generally based on a pure silicon alkoxide crosslinker $\text{Si}(\text{OR})_4$ and some organically modified silicate $\text{R}'\text{Si}(\text{OR}'')_3$ that will play the role of the functional monomer.

In most cases, tetraethyl orthosilicate (TEOS) is chosen as the crosslinker [58,59] but other crosslinkers such as tetramethyl orthosilicate (TMOS) can be used [34]. TEOS is usually preferred because the product of hydrolysis (ethanol) is less hazardous than the hydrolysis product of TMOS (methanol).

For the design of IIPs, some organosilanes compounds bearing functional groups that can bind metal ions are commercial such as (3-aminopropyl)trimethoxysilane (APTMS) [60], 3-(2-aminoethylamino)propyltrimethoxysilane (AAPTMS) [59], or 3-[2-(2-aminoethylamino)ethylamino]propyltrimethoxysilane (AAAPTMS) [58]. Ghanei-Motlagh et al. modified this last compound, AAAPTMS, by crosslinking it with epichlorohydrin around the target ion, Cd(II), to create an efficient chelating structure which was further crosslinked with TEOS to prepare the sol-gel corresponding IIP [58]. Modified functional organosilanes can also be synthesized to enhance the selectivity towards the template ion. For example, Güney et al. prepared a functional sol-gel precursor for the elaboration of a uranyl sensor by reacting 3-aminoquinoline with commercially available 3-isocyanatopropyl trimethoxysilane (ICTMS) [34].

In an original approach, Coelho et al. opted for a bifunctional hybrid imprinted polymer based on both sol-gel and FRP methods for the preparation of IIP-based carbon paste electrodes for Cd(II) determination [61]. For that purpose, they used an organosilane and vinyl functional monomers (3-mercaptopropyltrimethoxysilane (3-MPTMS) and 4-VP), associated to a silicon alkoxide and a FRP crosslinker (TEOS and TRIM) and to a hybrid crosslinker: 3-(trimethoxysilyl)propyl methacrylate (TMSPM) bearing an alkoxide and a vinyl moiety. The reason for such a complex system is that they proved in a preliminary work that this hybrid IIP exhibited a better selectivity and adsorption capacity than the corresponding pure organic (prepared by FRP) and inorganic (prepared by sol-gel) imprinted polymers [62].

There is an obvious interest in using sol-gel polymers because they can be directly applied on an electrode in the “sol” form before completing the polymerization in situ, thus giving rise to thin porous imprinted films [57]. However, it is worth noting that the use of this technique is currently being investigated for MIP-based sensors but remains confidential for the elaboration of IIP-based ones.

2.3. Surface imprinting of nanoparticles

The introduction of various functional materials, such as metallic or carbon-based nanoparticles has been identified as an efficient method to improve the sensitivity of molecularly imprinted electrochemical sensors through the enhancement of the surface area and/or the electroconductivity of the MIP layer [7]. For IIP-modified electrochemical sensors (IIEPCS), the major nanoparticles that are introduced in the polymer matrices are carbon nanotubes (CNTs), usually in the form of multi-wall carbon nanotubes (MWCNTs), and magnetic nanoparticles (MNPs) of magnetite Fe₃O₄. MWCNTs are used because of their large surface-to-volume ratio, high conductivity, good electron transfer catalytic property, and chemical stability [63]. As for MNPs, their interest lies in the possibility of taking advantage of the magnetic core to facilitate the separation of the modified particles during their

preparation or to immobilize them on an electrode [64]. However, some authors only use their high surface area property to enhance the IIPs adsorption capacities in the sensors [65].

To improve the compatibility between the IIP and the additional nanoparticle, surface imprinting technology can be introduced. It is based on the coverage of preformed particles by an IIP layer. The advantages of such surface imprinting technology are well-known: they include increased mass transfer efficiency, avoiding the target embedding phenomenon, and better interaction between the nanoparticle and the imprinted polymer [66]. It can also speed up the electron transfer between the analyte and the electrode.

To perform surface imprinting on MWCNTs, Mathew's group developed a 'grafting through' strategy by functionalizing the MWCNTs with allyl amine [67,68] or allyl alcohol [35,63,69] to introduce vinyl groups before the formation of the IIP shell by FRP (Fig. 2.C). On their part, Ghanei-Motlagh et al. simply embedded reduced graphene oxide (RGO) nanosheets by mixing these particles with the pre-polymerization mixture to obtain IIP modified RGO nanosheets without any chemical bond between RGO and the IIP [70].

Regarding MNP, they are typically prepared by co-precipitation of Fe(II) and Fe(III) ions [71] or by the solvothermal method [59]. In the first step, a silica layer is usually coated around the MNP to form a $\text{Fe}_3\text{O}_4@\text{SiO}_2$ core. Then, whereas Ghanei-Motlagh et al. simply mix those $\text{Fe}_3\text{O}_4@\text{SiO}_2$ particles with the pre-polymerization mixture to generate the IIP shell [64]. Dahaghin et al. introduce vinyl groups on the surface of the particles to bind the IIP shell via a 'grafting through' FRP step [71,72]. Similarly, An et al. modify Fe_3O_4 particles with 3-(trimethoxysilyl)propyl methacrylate to functionalize the surface of the particles by methacrylate groups [73]. Afkhami et al. also chemically graft an IIP layer onto $\text{Fe}_3\text{O}_4@\text{SiO}_2$ core but through a sol-gel procedure [59].

2.4. Crosslinking of linear chains

While most methods of IIP preparation rely on the well-established FRP or sol-gel methods described previously, some authors synthesize them by crosslinking linear polymer chains of chitosan in the presence of the template ion. The principle is similar to that of the first IIPs described by Nishide et al. in 1976 who crosslinked poly(4-vinylpyridine) with 1,4-dibromobutane [74]. Chitosan presents the advantage of being a bio-sourced polymer that can play the role of a macromolecular ligand through its amine and hydroxyl chelating groups.

In this way, Wu et al. report the preparation of an IIP based electrochemical sensor for Cr(VI) by crosslinking of chitosan with glutaraldehyde [75]. Wei et al. use epichlorohydrin to crosslink the chitosan chains for Cu(II) detection (Fig. 2.D) [36].

3. Preparation of IIP-modified electrochemical sensors

The determination of metal ions by IPECS is mainly based on classical potentiometry and voltammetry by taking advantage of the selectivity properties of IIPs. In the case of potentiometry, IIP (usually in a particle format) replace the classical ionophores used in ISE. For voltammetry, the role of IIP is to selectively accumulate the metallic ion.

Fig. 3 gives a brief overview of the different strategies that can be implemented to prepare IIP-modified electrodes based on the use of IIP either as particles or as films, in relation with the electrochemical detection method (potentiometry or voltammetry).

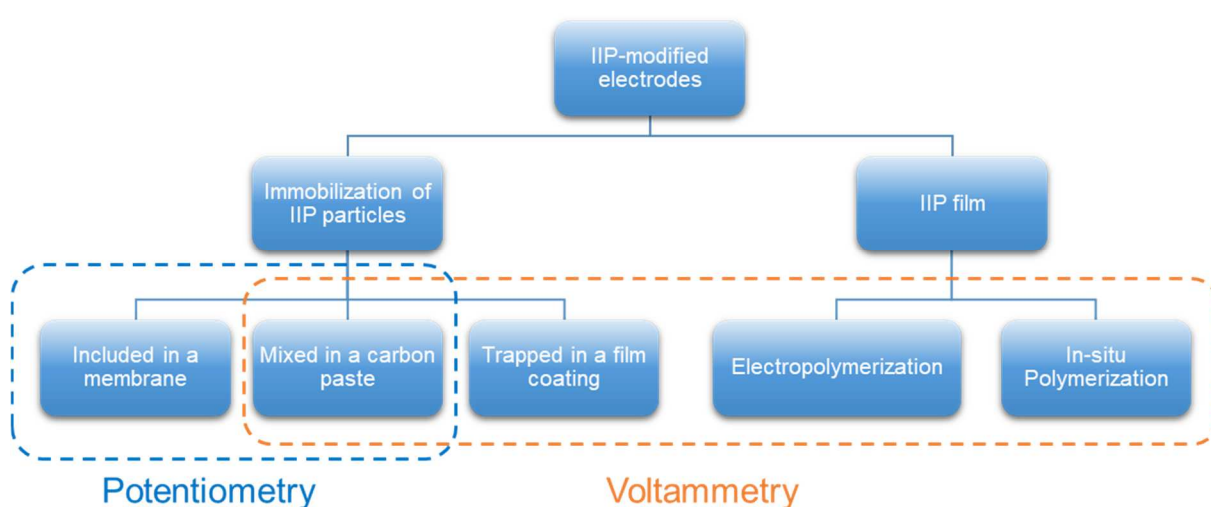


Fig. 3. Major pathways currently used to fabricate IIP-modified electrodes

3.1. Immobilization of IIP particles

3.1.1. Ion-selective membrane electrodes for potentiometry

While the field of ion-selective electrodes (ISE) for metal ion detection is now very mature, with decades of research and optimization, the development of IPECS for potentiometry is rather recent and has mainly focused on the feasibility of such sensors.

Two main types of membrane electrodes containing IIP particles have been developed as ISE: membrane electrodes with inner solution (Fig.4.A.) and all-solid-state (dip-coated) electrodes (Fig. 4.B.).

In the case of membrane electrodes with an inner filling solution, the measured potential is defined by the difference in potential at both phase boundaries (between the sample solution and the membrane and between the inner filling solution and the membrane). Thus, the difference in ion distribution in the sample and in the inner filling solution allows the measurement of a potential (Fig.4.A.)

For dip-coated electrodes (Fig. 4.B.), the potential measured can be described as the quantity of electrons accumulated at the interface. In this case, the electrode interface functions as a capacitor. In both instances, the membrane should have a special affinity for the target ion to allow its diffusion. For that reason, IIP particles with their binding affinity and high selectivity for specific target ions can play a major role in replacing ionophores in ISE.

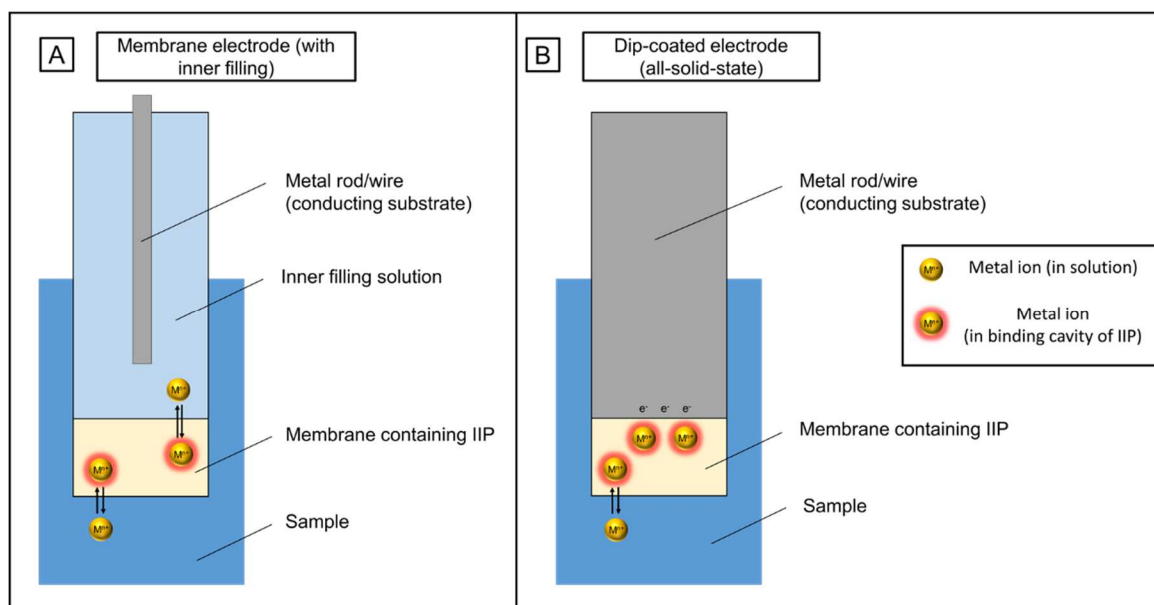


Fig. 4. The two main types of potentiometric ion-specific electrodes: A. Membrane electrodes with inner solution; B. Dip coated electrode (all-solid state).

In the reviewed literature, the IIP-modified membrane electrodes are mainly composed of a polyvinyl chloride (PVC) matrix, a plasticizer, and IIP particles. Anionic additives, such as sodium tetrphenylborate (NaTPB) and potassium tetrakis(4-chloro-phenyl) borate (KTpCIPB), are also commonly used to promote charge transfer in the membrane and reduce the impedance of the membrane, to ultimately enhance the signal.

The role of plasticizers is to impart the plastic membrane with the desired mechanical properties without crystallization and oxidation. However, it can also affect the selectivity and the limit of detection (LOD) [76]. That is why several authors optimize the composition of their membranes to maximize their performances. The optimal compositions used by the authors are reported in Table 1.

Table 1. Composition of membrane electrodes, limit of detection and linear range limit. DNP = dinonylphthalate; DBP = Dibutylphthalate; NPOE = 2-nitrophenyloctyl ether

Target ion	Composition				Analytical Performance		Ref.
	IIP Particles	Plasticizer	PVC	Additive	LOD (mol/L)	Linear range (mol/L)	
Ca(II)	11%	61% (DNP)	24%	4% (NaTPB)	7.50×10^{-7}	$1.00 \times 10^{-6} - 1.00 \times 10^{-1}$	[77]
Ni(II)	11%	64.5% (DBP)	21.4%	3% (NaTPB)	5.00×10^{-6}	$1.00 \times 10^{-5} - 1.00 \times 10^{-1}$	[78]
Cu(II)	4%	62.3% (DBP)	33.7%	-	2.00×10^{-6}	$1.00 \times 10^{-5} - 1.00 \times 10^{-1}$	[79]
As(III)	10.1%	64.5% (DNP)	21.4%	4% (NaTPB)	5.00×10^{-7}	$7.00 \times 10^{-7} - 1.00 \times 10^{-1}$	[80]
Ag(I)	9%	61.3% (DNP)	27.6%	1.9% (NaTPB)	1.00×10^{-6}	$5.00 \times 10^{-6} - 1.00 \times 10^{-1}$	[40]
Dy(III)	22%	50% (NPOE)	22%	6% (NaTPB)	2.00×10^{-6}	$8.00 \times 10^{-6} - 1.00 \times 10^{-1}$	[81]
Uranyl	22%	50% (NPOE)	22%	6% (NaTPB)	2.00×10^{-8}	$2.00 \times 10^{-8} - 1.00 \times 10^{-2}$	[82]
Uranyl	4%	62.3% (DBP)	33.7%	-	3.00×10^{-6}	$3.00 \times 10^{-5} - 6.00 \times 10^{-2}$	[83]

Another option, that has been implemented in the case of IPECS, is to prepare all-solid-state electrodes (Fig. 4.B.) which do not require an internal filling. In this instance, the metal wire is simply dip-coated with a membrane of similar composition to the ones used in the previous section. Shamsipur et al. and Abu-Dalo et al. use the same membrane formulations (Table 1) to make all-solid-state electrodes (Table 2) [40,83]. However, as can be seen from Table 2, the composition of the membrane remains relatively similar to those used in membrane electrodes.

Table 2. Composition of all-solid-state electrodes using PVC as the matrix

* Electrode was first coated with polyaniline, followed by coating of MWCNT trapped in Nafion and then coated with IIP-PVC membrane.

Target ion	Composition				Analytical Performance		Ref.
	IIP Particles	Plasticizer	PVC	Additive	LOD (mol/L)	Linear range (mol/L)	
Cu(II)	4%	69% (NPOE)	26%	1% (KTpCIPB)	7.60×10^{-7}	$1.00 \times 10^{-6} - 1.00 \times 10^{-1}$	[84]
Cu(II)	4%	69% (NPOE)	26%	1% (KTpCIPB)	8.40×10^{-7}	$1.00 \times 10^{-6} - 1.00 \times 10^{-1}$	[85]
Ag(I)	9.2%	61.3% (NPOE)	27.6%	1.9% (NaTPB)*	1.20×10^{-9}	$3.20 \times 10^{-9} - 1.00 \times 10^{-1}$	[40]
Cd(II)	21%	43% (NPOE)	21%	15% (NaTPB)	1.00×10^{-7}	$2.00 \times 10^{-7} - 1.00 \times 10^{-2}$	[86]
Uranyl	4%	62.3% (DBP)	33.7%	-	5.00×10^{-6}	$1.00 \times 10^{-5} - 5.00 \times 10^{-2}$	[83]

All-solid-state electrodes are easy to implement but have the disadvantage of signal drift that can occur due to the low contact area between the membrane and the electrode [31]. One possibility to solve this problem is to cover the electrode surface with a conducting polymer [31]. Thus, Shamsipur et al. manage to lower the LOD of IIP-PVC-membrane electrodes by adding polyaniline and MWCNT trapped in a Nafion® layer on a graphite electrode before coating with an IIP-PVC-membrane [40].

3.1.2. Carbon paste electrodes for potentiometry

Another class of IPECS that have been used as ISE are Carbon Paste Electrodes (CPE). While they have been classified as liquid membrane type electrodes [87], they considerably differ from the previously described PVC membrane electrodes because they are mainly composed of graphite carbon paste. In the case of IPECS, IIP are added for the same purpose as in the previous section: to replace conventional ionophores. One of the main reasons explaining the wide use of modified CPE is their fairly simple preparation process. Typically, graphite is mixed with a binder (such as paraffin oil) and the IIP particles in a mortar with a pestle to form the carbon paste. With the aim of creating an effective solid contact between the core electrode and the carbon paste, a possibility is to introduce high surface area additives (such as nanoparticles) in the carbon paste (Table 3). That is why authors describe the use of conducting additives such as SWCNT [41,55,88], Graphene Nano Sheets (GNS) [89,90] or graphitic carbon nitride nanosheets (g-C₃N₄) [53]. However, other less commonly used additives with high surface areas are also described such as alumina nanoparticles [91] and nano silica [41,88]. It should be noted that a higher surface area also supposedly enhances the extraction capabilities of the carbon paste.

In the preparation of the carbon paste, the binder can also be replaced by ionic liquids: 1-*n*-butyl-3-methylimidazolium tetrafluoroborate ([bmim]BF₄) [41,88] or 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl) imide ([BMP]Tf₂N) [89,90]. Ganjali et al. report a better linear range when replacing paraffin oil with an ionic liquid due to its greater dielectric constant [41].

The exact formulation for the carbon pastes used in the preparation of IPECS for potentiometry can be found in Table 3. In most cases, the composition was optimized empirically to enhance the performance of the electrode.

Table 3. Composition of carbon paste electrodes (CPE) for potentiometry

Target ion	Composition				Analytical Performance		Ref.
	IIP Particles	Graphite powder	Oil	Additives	LOD (mol/L)	Linear Range (mol/L)	
Cu(II)	20%	65% (graphite oxide)	10% (Paraffin oil)	5% (MWCNT)	4.00 x 10 ⁻⁷	1.00 x 10 ⁻⁶ - 1.00 x 10 ⁻¹	[55]
Zn(II)	8%	60%	20% (BMPTf ₂ N)	12% (GNS@Ag NPs)	2.95 x 10 ⁻⁹	4.01 x 10 ⁻⁹ - 1.00 x 10 ⁻²	[90]
Cd(II)	20%	54%	20% ([bmim]BF ₄)	5% (MWCNT), 1% (Nano-silica)	1.00 x 10 ⁻⁷	1.00 x 10 ⁻⁷ - 1.00 x 10 ⁻²	[41]
Hg(II)	15%	69%	10% ([bmim]BF ₄)	5% (MWCNT), 1% (Nano-silica)	1.00 x 10 ⁻⁷	1.00 x 10 ⁻⁷ - 1.00 x 10 ⁻²	[88]
Hg(II)	14%	53%	20% (BMPTf ₂ N)	10% (GNS) & 3% (Alumina Nano-particles)	1.95 x 10 ⁻⁹	4.00 x 10 ⁻⁹ - 1.30 x 10 ⁻³	[89]
Hg(II)	5%	65%	25% (nujol oil)	5% (g-C ₃ N ₄)	4.30 x 10 ⁻¹⁰	1.00 x 10 ⁻⁹ - 1.00 x 10 ⁻³	[53]

3.1.3. Carbon paste electrodes for voltammetry

CPE are also used widely in voltammetric sensors and are prepared following the same basic procedure presented in the previous section. Some authors show that the addition of conductive additives such as MWCNT [43,47,52,92,93], g-C₃N₄ [51], carbon nanotubes [94,95], or ionic liquid [39] improves the performance of the sensor. Alizadeh et al. show that adding CNT to a carbon paste with IIPs increased the signal almost 3 times [52]. However, CPE can also be used without additives and still reach low LOD. Table 4 presents all the best formulations used for voltammetric CPE optimized by authors in terms of performance.

An original way to immobilize IIP particles on an electrode is described by Ghanei-Motlagh et al. who take advantage of the magnetic properties of IIP modified MNP to couple IIP particles and electrochemical analysis [64]. The magnetic IIP particles are separated with a magnet, and recovered on an electrode surface equipped with a magnet (Fig. 5). In this strategy, the carbon paste is not mixed with IIP particles. An advantage of the magnetic properties of the IIP is the possibility to clean and reuse the CPE very easily.

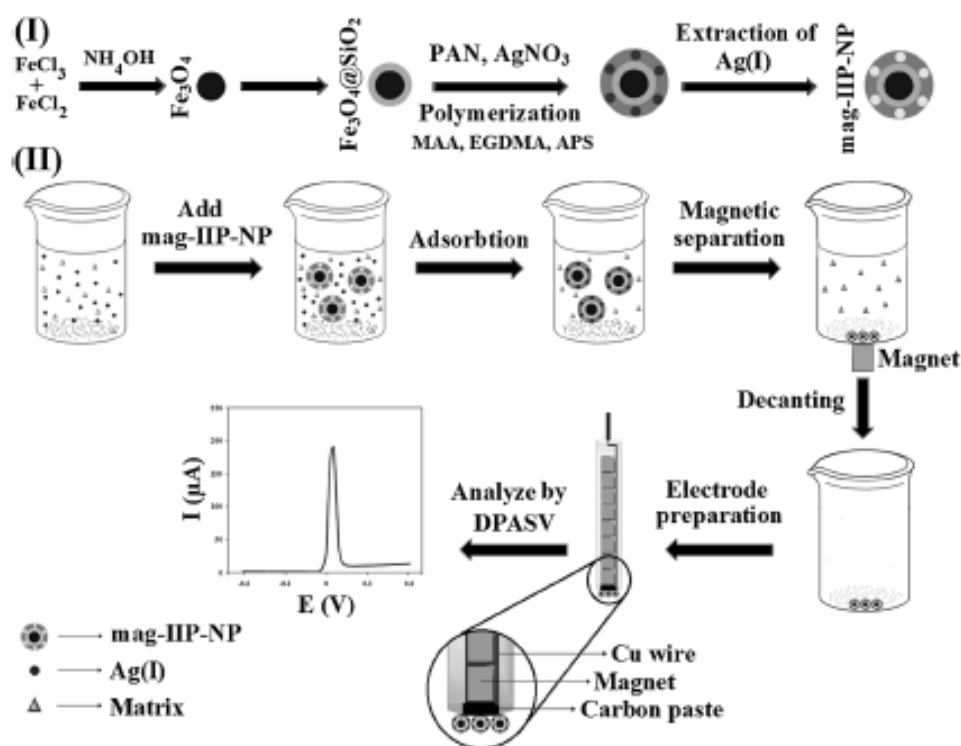


Fig. 5. Coupling a Carbon Paste Electrode and Magnetic IIP Nanoparticles for the selective adsorption and analysis of the target analyte (Reprinted by permission from Springer-Verlag, Copyright 2017 [64])

Table 4. Composition of CPE used in voltammetry, linear detection and linear range limits. P.O. = paraffin oil; S.O. = silicon oil; M.O. = mineral oil; n-eic. = *n*-eicosane; I.L. = ionic liquid

Target ion	Composition				Analytical Performance		Ref.
	IIP	Graphite	Oil	Additive	LOD (mol/L)	Linear Range (mol/L)	
Cr(III)	4%	82%	14% (n-eic.)	-	1.76×10^{-8}	$1.00 \times 10^{-7} - 1.00 \times 10^{-5}$	[96]
Cu(II)	4%	77%	19% (P.O.)	-	2.30×10^{-8}	$7.00 \times 10^{-8} - 1.00 \times 10^{-4}$	[97]
Cu(II)	15%	51%	29% (S.O.)	5% (MWCNT)	5.35×10^{-9}	$3.15 \times 10^{-8} - 1.89 \times 10^{-6}$	[43]
Mo(VI)	15%	75% (Graphite + PO mixture)		-	4.17×10^{-10}	$2.08 \times 10^{-9} - 5.21 \times 10^{-6}$	[59]
Pd(II)	15%	55%	30% (P.O.)	-	3.00×10^{-12}	$1.00 \times 10^{-11} - 1.00 \times 10^{-6}$	[98]
Ag(I)	13%	66%	21% (n-eic.)	-	9.00×10^{-10}	$2.80 \times 10^{-9} - 8.50 \times 10^{-7}$	[40]
Ag(I)	5%	63%	27% (P.O.)	5.2% (MWCNT)	1.20×10^{-10}	$5.00 \times 10^{-10} - 2.80 \times 10^{-7}$	[47]
Ag(I)	/	73%	27% (P.O.)	-	1.39×10^{-10}	$4.64 \times 10^{-10} - 1.39 \times 10^{-6}$	[64]
Cd(II)	13%	58%	29% (n-eic.)	-	5.20×10^{-10}	$1.00 \times 10^{-9} - 5.00 \times 10^{-7}$	[12]
Cd(II)	15%	56%	29% (S.O.)	-	2.76×10^{-9}	$1.78 \times 10^{-8} - 1.78 \times 10^{-6}$	[99]
Cd(II)	26%	61%	14% (M.O.)	-	4.40×10^{-8}	$8.98 \times 10^{-8} - 5.95 \times 10^{-5}$	[61]
Cd(II)	10%	65%	25% (P.O.)	-	1.33×10^{-9}	$4.45 \times 10^{-9} - 3.56 \times 10^{-7}$	[58]
Hg(II)	16%	63%	22% (n-eic.)	-	5.20×10^{-10}	$2.50 \times 10^{-9} - 5.00 \times 10^{-7}$	[100]
Hg(II)	12%	58%	20% (P.O.)	10% (I.L.)	1.00×10^{-10}	$5.00 \times 10^{-10} - 1.00 \times 10^{-8}$ and $8.00 \times 10^{-8} - 2.00 \times 10^{-6}$	[39]
Hg(II)	13%	63%	25% (P.O.)	-	1.99×10^{-10}	$9.97 \times 10^{-10} - 7.98 \times 10^{-6}$	[101]
Hg(II)	7%	75%	14% (n-eic.)	4% (MWCNT)	2.90×10^{-11}	$1.00 \times 10^{-10} - 2.00 \times 10^{-8}$	[52]
Hg(II)	8%	76%	11% (M.O.)	5% (g-C3N4)	1.80×10^{-11}	$6.00 \times 10^{-11} - 2.50 \times 10^{-8}$	[51]
Tl(I) & Tl(III)	5%	61%	29% (S.O.)	5% (CNT)	3.72×10^{-9}	$1.47 \times 10^{-8} - 1.17 \times 10^{-6}$	[94]
Pb(II)	13%	58%	29% (n-eic.)	-	6.00×10^{-10}	$1.00 \times 10^{-9} - 8.10 \times 10^{-7}$	[102]
Pb(II)	15%	55%	30% (P.O.)	-	1.00×10^{-10}	$3.00 \times 10^{-10} - 1.00 \times 10^{-9}$ and $1.00 \times 10^{-8} - 1.00 \times 10^{-6}$	[42]
Pb(II)	15%	55%	30% (P.O.)	-	3.00×10^{-11}	$1.00 \times 10^{-10} - 1.00 \times 10^{-5}$	[46]
Pb(II)	7%	55%	27% (P.O.)	10% (MWCNT)	2.41×10^{-9}	$1.45 \times 10^{-8} - 2.65 \times 10^{-7}$	[92]
Pb(II)	20%	50%	30% (P.O.)	-	1.30×10^{-11}	$1.00 \times 10^{-9} - 7.50 \times 10^{-7}$	[103]
Bi(III)	10%	63%	22% (n-eic.)	5% (CNT)	8.90×10^{-9}	$2.00 \times 10^{-7} - 2.00 \times 10^{-6}$	[95]
Ce(III)	3%	68%	22% (n-eic.)	7% (MWCNT)	1.00×10^{-11}	$2.50 \times 10^{-11} - 1.00 \times 10^{-6}$	[93]
Ce(III)	5mg	20mg	"a certain amount" P.O.	-	1.50×10^{-7}	$1.00 \times 10^{-6} - 2.00 \times 10^{-4}$	[104]
Eu(III)	6%	78%	16% (n-eic.)	-	1.50×10^{-7}	$5.00 \times 10^{-7} - 3.00 \times 10^{-5}$	[105]
Uranyl	10%	60%	30% (P.O.)	-	1.11×10^{-10}	$3.70 \times 10^{-10} - 3.70 \times 10^{-5}$	[106]
Uranyl	15%	55% (carbon powder)	30% (P.O.)	-	3.07×10^{-10}	$2.00 \times 10^{-9} - 3.00 \times 10^{-7}$	[34]
Uranyl	?	80.00%	20% (S.O.)	graphene	1.81×10^{-9}	$1.00 \times 10^{-10} - 1.00 \times 10^{-7}$	[60]

3.1.4. IIP particles immobilized in film coating on electrode surface

3.1.4.1. IIP particles trapped in film coating

IIP-modified electrodes can also be made by dispersing IIP particles in a film-forming matrix. For this, some authors use Nafion® as it is a stable film-forming polymer commercially available. One of the issues encountered when using this product is that the thickness of the film is hard to control. If it is too thick it may act as an insulator and decrease the signal when used in electrochemical sensors [107]. To counterbalance this drawback, most authors use an additive either to increase conductivity and/or to increase the contact area between the electrode, the IIP and the film-forming matrix. Tarley et al. cast a mixture of IIP and MWCNT on the electrode surface followed by the application of a Nafion® solution before leaving it to dry to form the IIP-modified Nafion®-film [44]. Similarly, some authors use IIP-modified MWCNT [35,63,67–69] or IIP-modified-RGO [70] particles, synthesized by surface imprinting, to improve the conductivity in the Nafion® film.

Velempini et al. suggest to first electropolymerize a coating of polypyrrole (PPy) before applying the dispersion of IIP-Nafion® [50]. In this case, PPy is also used to improve conductivity and contact area between the different components.

However, Nafion® is not the only option to make a film on an electrode. For instance, Prasad et al. use a sol-gel as a film-former to trap the IIP particles on the electrode. In this situation, the mixture of sol-gel, IIP and conducting additive were mixed and spin-coated on the surface of the electrode [54]. Carbon black was used as an additive to prevent electrode insulation but also to prevent shrinkage of the sol-gel film.

Hu et al. use chitosan as a film-forming to set the IIP instead of Nafion® or a sol-gel [108]. Contrary to the previous cases no additive was used, so they optimized the amount of chitosan to maximize the performance. However, it is clear from the data in Table 5, that this is not the best sensor when it comes to LOD probably due to the absence of electroconducting additive.

Table 5. Composition, limit of detection and linear range limits of IIPs trapped in film coating on electrodes

Target ion	Composition			Analytical Performance		Ref.
	IIP-modified Nano-Particles	Additive mixed with IIP Particles	Film-forming	LOD (mol/L)	Linear range (mol/L)	
Cr(III)	IIP-MWCNT	-	Nafion	5.10×10^{-8}	$1.92 \times 10^{-5} - 9.62 \times 10^{-5}$	[67]
Mn(II)	IIP-MWCNT	-	Nafion	1.38×10^{-8}	$1.82 \times 10^{-5} - 9.10 \times 10^{-5}$	[68]
Co(II)	IIP-MWCNT	-	Nafion	1.01×10^{-11}	$1.70 \times 10^{-5} - 8.48 \times 10^{-5}$	[35]
Zn(II)	IIP-MWCNT	-	Nafion	1.32×10^{-10}	$1.53 \times 10^{-5} - 7.65 \times 10^{-5}$	[63]
Hg(II)	IIP-RGO	-	Nafion	9.97×10^{-11}	$3.49 \times 10^{-10} - 3.99 \times 10^{-7}$	[70]
Hg(II)	IIP Particles	Predeposited Ppy film	Nafion	4.99×10^{-10}	$9.97 \times 10^{-8} - 3.99 \times 10^{-6}$	[50]
Pb(II)	IIP-MWCNT	-	Nafion	2.00×10^{-8}	$4.83 \times 10^{-6} - 2.41 \times 10^{-5}$	[69]
Pb(II)	IIP Particles	MWCNT	Nafion	7.72×10^{-10}	$2.41 \times 10^{-9} - 5.79 \times 10^{-8}$ and $7.24 \times 10^{-8} - 1.06 \times 10^{-7}$	[44]
Cu(II)	IIP Particles	Carbon Black	Sol-gel	5.35×10^{-10}	$1.97 \times 10^{-9} - 2.83 \times 10^{-8}$	[54]
Cd(II)	IIP Particles	Carbon Black	Sol-gel	4.45×10^{-10}	$1.11 \times 10^{-9} - 5.29 \times 10^{-8}$	[54]
Pb(II)	IIP Particles	-	Chitosan	1.00×10^{-8}	$5.00 \times 10^{-8} - 6.00 \times 10^{-5}$	[108]

3.1.4.2. Miscellaneous immobilization of IIP particles on electrode surface

Some authors describe the simple 'casting' of IIP particles directly on the electrode. Rajabi et al. and Razmi et al. both disperse the IIP particles in a solvent, apply them on an electrode and leave them to dry [48,109]. As has already been stated, IIPs can often act as insulators especially if the polymer thickness is not controlled. To circumvent this, an electroconducting additive can be used. Rajabi et al. mix the polymer particles with MWCNT before applying [48]. Razmi et al use an IIP based on polydopamine which is itself electroconducting [109]. On the other hand, Roushani et al. first apply a conducting film composed of a mixture of chitosan, ionic liquid and MWCNT on the electrode surface. More than just improving the conductivity, this film which presents a large specific surface area also increases the loading surface of the electrode for the immobilization of the IIP particles [45].

Several authors also describe the use of IIP-modified magnetic nanoparticles that are synthesized and then cast directly on the electrode [71–73,110]. While they do not use conductive additives such as the ones presented previously, the use of modified IIP-MNPs may help to enhance the signal obtained with these electrodes by increasing the contact area and the adsorption capacity [71].

The main issue with simply applying the polymers on the electrode surface is that there is no certainty that the polymers will remain on the electrode after reuse or washing steps. Meaning that over time the modified electrodes may lose IIP particles and thus have poor reusability as well as reproducibility. To overcome this problem, Di Masi et al. report the modification of gold electrodes by using the "grafting to" method [111]. They use cysteamine to form a Self-Assembled Monolayer (SAM). Carboxylic acid-functionalised IIP nanoparticles then react with the amine groups of cysteamine to achieve the grafting of the IIP directly at the electrode surface. In this way, the polymer is properly "anchored" to the electrode.

Table 6. Composition, limit of detection and linear range limits of electrodes where IIP particles were immobilized on electrode surface

Target ion	Fabrication		Analytical Performance		Ref.	
	IIP-modified Nano-Particles	Additive mixed with IIP Particles	Deposition of IIP particles on electrode	LOD (mol/L)		Linear range (mol/L)
Mn(II)	IIP Particles	MWCNT - Chitosan - Ionic Liquid	Casting suspension of MWCNT - Chitosan and Ionic Liquid, casting suspension of IIP particles	1.50×10^{-7}	2.00×10^{-6} - 9.00×10^{-6}	[45]
Ni(II)	IIP Particles	-	Casting suspension of electroconducting IIP particles (polydopamine)	3.90×10^{-7}	1.00×10^{-6} - 2.50×10^{-5}	[109]
Cu(II)	IIP-MNP	-	Casting of IIP@MNP suspension	5.99×10^{-6}	1.00×10^{-5} - 1.00×10^{-3}	[73]
Cu(II)	IIP Particles	-	Cysteamine SAM on gold electrode, Coupling with NH ₂ -modified IIP	7.4×10^{-11}	1.90×10^{-9} - 6.10×10^{-8}	[111]
Cd(II)	IIP-MNP	-	Casting IIP@MNP suspension	1.00×10^{-10}	8.00×10^{-9} - 8.00×10^{-7}	[72]
Hg(II)	IIP Particles	MWCNT	Casting suspension of IIP particles and MWCNT	5.00×10^{-9}	1.00×10^{-8} - 7.00×10^{-4}	[48]
Pb(II)	IIP-MNP	-	Casting of IIP@MNP suspension	2.41×10^{-10}	4.83×10^{-10} - 3.86×10^{-7}	[71]

3.2. Electrodes modified with IIP film

3.2.1. Electropolymerization: modification of electrodes

A method that can be used for the *in-situ* formation of a film directly on the electrode is electropolymerization. The principle behind this polymerization is simple. The working electrode is dipped in a monomer solution and by applying several cyclic scans in a certain potential range (depending on the monomer) a polymer is obtained directly at the electrode surface [112]. One of the advantages of this method is that the so-formed polymer film is not insulating which facilitates the transfer of electrons compared to other *in-situ* polymerization methods. Pyrrole [113], phenylenediamine [114] and mercaptobenzotriazole [15] are commonly used to prepare IIP films by electropolymerization. The major results with electrodes prepared by this technique are given in Table 7. Nanoparticles are often added to the polymerization mixture in order to increase the conductivity and/or the surface area.

The approach of Fu et al. is slightly different because they first modify nanoparticles with electropolymerizable monomers. In a first article, they describe the use of mercaptobenzotriazole-capped SiO₂ particles [15]. After the electropolymerization step in presence of Hg(II) template, the etching of silica generated a highly porous and efficient conducting film. In another work, they use gold particles that can form an Au-thiol bond with the thiol moiety of the mercaptobenzotriazole monomer as illustrated in Fig.6. [115].

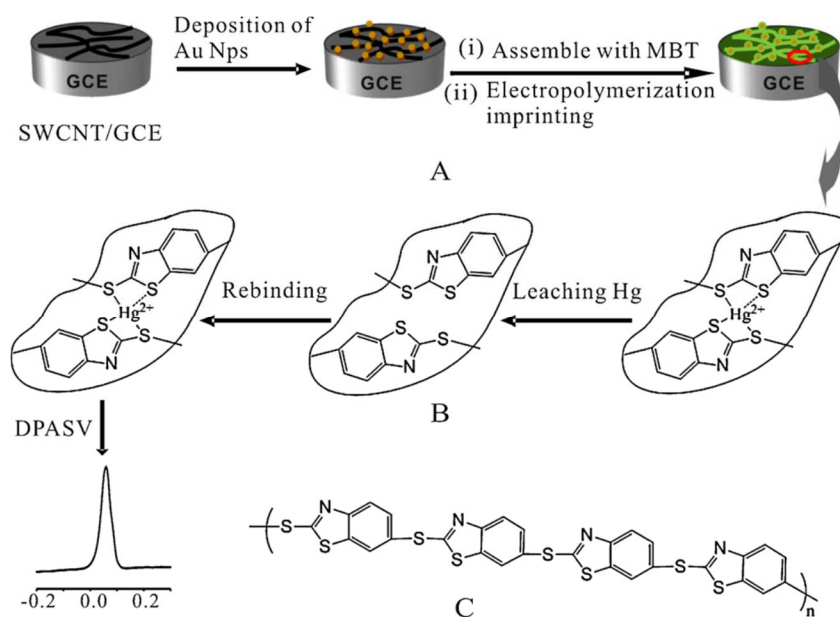


Fig. 6. Preparation of Hg(II)-imprinted electropolymer with Au nanoparticles and SWCNT (Reprinted by permission from Elsevier, Copyright 2012 [115])

While in most cases described so far the amount of target ion is directly measured through its own electrochemical response, Ma et al suggest a method allowing the indirect determination of As(III) [116]. They first incubate the electrode in a solution containing the target ion and then record the cyclic voltammogram of a ferricyanide/ferrocyanide solution, the peak current decreases when the adsorbed As(III) increases.

Table 7. Composition, limit of detection and linear range limits of electrodes obtained by electropolymerization

Target ion	Electrochemical Method	Composition		Analytical Performance		Ref.
		Monomer	Additive	LOD (mol/L)	Linear range (mol/L)	
As(III)	CV	<i>p</i> -phenylenediamine	Nano-porous Gold	7.1×10^{-12}	$2.0 \times 10^{-11} - 9.0 \times 10^{-9}$	[116]
Cu(II)	Potentiometry	pyrrole/methyl red	/	5.00×10^{-7}	$3.90 \times 10^{-6} - 5.00 \times 10^{-2}$	[117]
Cu(II)	DPASV	pyrrole/methyl red	/	6.50×10^{-9}	$1.00 \times 10^{-8} - 1.00 \times 10^{-3}$	[117]
Cu(II)	DPV	<i>p</i> -phenylenediamine	/	2.70×10^{-9}	$9.50 \times 10^{-10} - 2.44 \times 10^{-7}$	[114]
Cd(II)	SWASV	<i>o</i> -phenylenediamine	RGO	1.16×10^{-9}	$8.90 \times 10^{-9} - 4.45 \times 10^{-7}$	[118]
Cd(II)	SWASV	pyrrole	RGO	2.31×10^{-9}	$8.90 \times 10^{-9} - 8.90 \times 10^{-7}$	[113]
Hg(II)	SWASV	mercaptobenzotriazole-capped SiO ₂ particles	/	1.00×10^{-10}	$1.00 \times 10^{-9} - 1.60 \times 10^{-7}$	[15]
Hg(II)	DPASV	mercaptobenzotriazole	SWCNT/Gold particles	8.00×10^{-11}	$4.00 \times 10^{-10} - 9.60 \times 10^{-8}$	[115]

3.2.2. *In-situ* polymerization

In this section, the described IIP films are not prepared by electropolymerization. Instead the *in-situ* polymerisation is carried out by spin-coating or dip-coating an electrode with a pre-polymerisation mixture and then carrying out the polymerisation by methods previously described such as FRP or

crosslinking of polymer chains. The composition and main results of these electrodes are presented in Table 8.

In contrast to polymers obtained by electropolymerization, the polymers discussed in this section are not typically conducting. For this reason, most authors performing *in-situ* polymerization include a conductive additive in the pre-polymerization mixture. For instance, Kumar et al. add MWCNT to the monomer, crosslinker and initiator mixture which is then spin-coated on the electrode and polymerised to form an IIP film [119]. Other authors use different conducting additives such as graphene [75,120] or graphene oxide [36] either before or when applying the pre-polymerization mixture.

Prasad et al. and Torkashvand et al. describe the use of IIP-MNP films on electrodes. They do this by first drop-coating the MNP and then spin-coating on top of this [65] or simply incubating the electrode with the pre-polymerization mixture [110]. *In-situ* polymerization is then carried out to form an IIP-MNP film.

Table 8. Composition, limit of detection and linear range limits of electrodes fabricated with in-situ polymerization

Target ion	Composition			Analytical Performance		Ref.
	IIP-modified Nano-Particles	Additive mixed with IIP Particles	In-situ polymerization or IIP Particles	LOD (mol/L)	Linear range (mol/L)	
Cr(VI)	-	Graphene	Electrodeposition of Graphene and prepolymerization mixture, polymerization with glutaraldehyde	6.40×10^{-10}	$1.00 \times 10^{-9} - 1.00 \times 10^{-5}$	[75]
Co(II)	MNP	-	Coating electrode with modified MNP followed by in-situ polymerization	1.00×10^{-10}	$5.00 \times 10^{-10} - 5.00 \times 10^{-7}$	[110]
Cu(II)	-	-	Spin-coating and in-situ polymerization (OMNIIP)	2.83×10^{-11}	$1.26 \times 10^{-10} - 1.23 \times 10^{-7}$	[56]
Cu(II)	-	Graphene oxide	Deposition of Graphene Oxide and prepolymerization mixture, polymerization with epichlorhydrin	1.50×10^{-7}	$5.00 \times 10^{-7} - 1.00 \times 10^{-4}$	[36]
Cu(II)	-	MWCNT	MWCNT and prepolymerization mixture spin coated and in-situ polymerization	2.50×10^{-10}	$1.54 \times 10^{-9} - 3.75 \times 10^{-7}$	[119]
Zn(II)	-	MWCNT	MWCNT and prepolymerization mixture spin coated and in-situ polymerization	4.21×10^{-10}	$1.50 \times 10^{-9} - 3.64 \times 10^{-7}$	[119]
Gd(III)	MNP	-	Spin-coating and in-situ polymerization	1.21×10^{-10}	$4.71 \times 10^{-9} - 6.02 \times 10^{-8}$	[65]
Ce(IV)	MNP	-	Spin-coating and in-situ polymerization	5.00×10^{-10}	$1.78 \times 10^{-9} - 4.45 \times 10^{-8}$	[65]

4. Performances and applications of sensors

4.1. Optimization of analytical parameters

In section 3, the optimization of the composition of the IIP-modified electrodes for potentiometry (amount of IIP, type and amount of plasticizer, ...) and voltammetry (amount of IIP, electroconducting

additives, ...) was discussed. This sub-section is devoted to the optimization of the experimental analytical conditions under which the measurements are performed. As was previously stated, the advantage of using IPECS is that they can improve the selective adsorption of the target ion. This is why most optimization of IPECS relates to the optimization of the adsorption of the target ion. Regardless of the method, the pH of the sample solution should be optimized as the adsorption of the metal ion by the IIP is pH-dependent because its binding capacity is affected by the protonation of its chelating groups [12,39].

In the case of potentiometric measurements, one of the main factors that requires optimization for potentiometric measurements is the conditioning of the electrode before use. For this reason, Topcu et al., who prepared graphite oxide-IIP electrodes for Cu(II) detection, studied the effect of different conditioning solutions and of the conditioning time to get a correct Nernstian behaviour [55]. In the case of membrane electrodes, the detection limit is also highly dependent on the inner solution composition and its target ion concentration. Thereby, Metilda et al. added EDTA or Na₂CO₃ as complexing agents of uranyl ion in the internal filling solution to decrease the concentration of this ion at the inner membrane surface and to optimize their IIP-modified electrode performances [82].

Fig. 7 illustrates the role of IIP in the case of IPECS used in voltammetry: in a first step, the IIP allows the selective extraction of the target ion on the modified electrode surface. Then the measurement is carried out, preceded by a reduction step in the case of stripping voltammetry. The role of the IIP is to prevent the possible obscuring of the signal of the target ion by the signal of interfering ions. Thus the extraction step can prove crucial to obtaining reliable results in very complex matrixes. This is why it is important to optimize the extraction time [75,96] and the stirring speed during the extraction step [98,100]. Commonly, an increase of the measured intensity is observed with increasing incubation time before reaching a maximum value: the start time of this plateau will be considered as the optimum practical value [75,96]. The extraction step can be followed by a washing step, to further remove lightly bound interfering ions [12]. In a similar fashion, in the case of stripping voltammetry, the signal intensity can also be increased by optimizing the reduction step (electrochemical accumulation time [40,58] and electrochemical accumulation potential [40,110]).

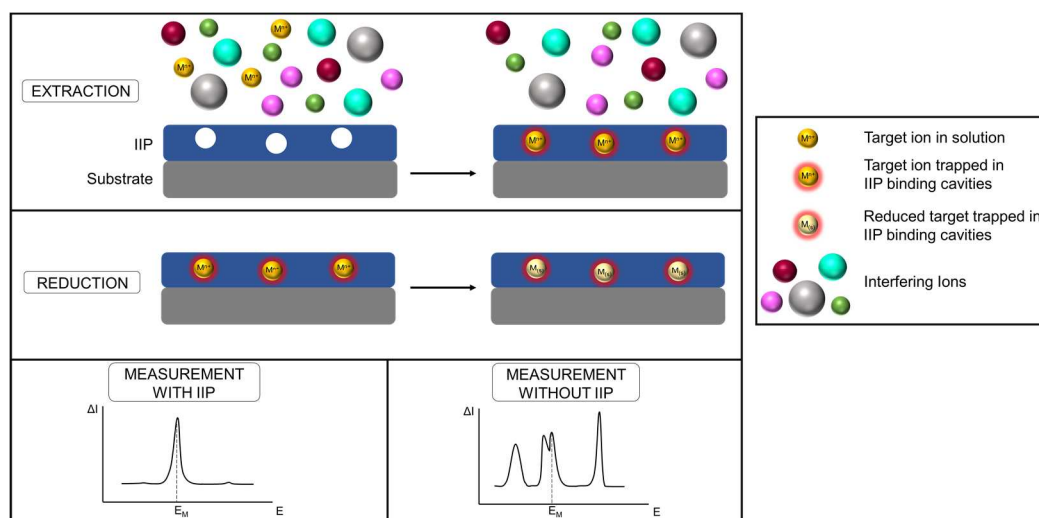


Fig. 7. Different steps for stripping voltammetry using an IIP-modified electrode (selective extraction, reduction and stripping)

4.2. Evaluation of the performances of IIP-modified sensors

As for all electrochemical sensors, the evaluation of the analytical performances of IPECS usually goes through the determination of their LOD and their linear range. Therefore, these values are systematically reported in the different tables presented in this review. For voltammetry, the best IPECS can present LOD as low as a few pmol/L. Bojdi et al. report an IIP-modified carbon paste electrode with a LOD of 3 pmol/L [98]. Alizadeh et al. and Luo et al. also worked CPEs with low LODs of 10 and 13 pmol/L, respectively [93,103]. Other methods of IPECS fabrication have also allowed to reach low LODs: Sebastian et al. report an IPECS with a LOD of 10 pmol/L by trapping IIP particles in a Nafion film [35], while Fu et al. managed to reach LODs of 100 pmol/L by electropolymerizing the IIP-film directly on the electrode [15]. These results make IPECS excellent candidates for the detection of metal ultra-trace in environmental conditions. On the other hand, IIP-modified membrane electrodes for potentiometric measurements currently show limited results with LODs closer to the 100 nmol/L range, one notable exception is Shamsipur et al. who presented a dip-coated electrode with a LOD of approximately 1.2 nmol/L. In this case, the electrode was first coated with polyaniline followed by a coating of MWCNT trapped in Nafion, which allowed to reach lower LODs [40]. CPE used in potentiometry seem to be superior to IIP-modified membrane electrodes as they can reach slightly lower detection limits, with Khazaei et al. presenting a CPE using IIPs and $g\text{-C}_3\text{N}_4$ as additives with a LOD of 430 pmol/L [53]. Although the voltammetric IPECS seem to be more sensitive than the potentiometric ones, the latter present wider linear ranges, offering the possibility of analysing more polluted samples.

While, some authors compare the performances of their IPECS to other types of electrodes used with the same electrochemical method and highlight the positive impact of the incorporation of IIP on the

LOD [35,43,93,98,103]. In the particular case of IPECS, there is an additional will to assess an imprinting effect that justifies the use of IIP. This is usually done by comparing the intensity of the IPECS electrochemical signal with that of a NIP-based sensor (NIPECS). NIP are non-imprinted polymers that are commonly prepared to play the role of control polymer because they are synthesized under the same conditions as the corresponding IIPs (monomers, composition, temperature...) except for the lack of the template ion. The absence of any specific binding cavities within the NIP is expected to reduce its binding capacity compared to that of the IIP and thus reduce the electrochemical response of the corresponding sensor.

As an example, Metilda et al. prepared three PVC-membrane electrodes for potentiometry with IIP particles, NIP particles and a "blank" electrode and compared their potential responses to increasing concentrations of the target uranyl ions [82]. While the blank electrode presented no sensitivity to the uranyl ions, both the IIP and NIP presented a Nernstian response (with a slope of 29.0 mV, as expected for a divalent cation). The imprinting effect was highlighted by the wider linear ranges obtained in the case of IPECS compared to NIPECS and by the lower LOD (2.10^{-8} M for the best IPECS composition, compared to 5.6×10^{-5} M for the best NIPECS composition).

For their IPECS voltammetric sensor, Shamsipur et al. first prepared IIP and NIP nanobeads that exhibit an imprinting factor (defined as the ratio of the maximum binding capacity of the IIP over that of the NIP) close to 3 for the template ion Ag(I) [40]. Then they incorporated these particles inside CPE and compared the anodic peak currents of the differential pulse stripping voltammograms (Fig. 8.A). The intensity measured in presence of Ag(I) was the lowest for the plain CPE (without any additive) and increased gradually with the addition of NIP and IIP. The imprinting factor (defined as the ratio of the anodic peak current of the IIP over that of the NIP) is close to 2.7, which is in agreement with the characterization of the polymer nanobeads. They further established a calibration curve by the addition of increasing amounts of Ag(I) and determined a LOD of 0.90 nM with a linear relationship between the intensity and the Ag(I) concentration from 2.8 to 850 nM (Fig.8.B).

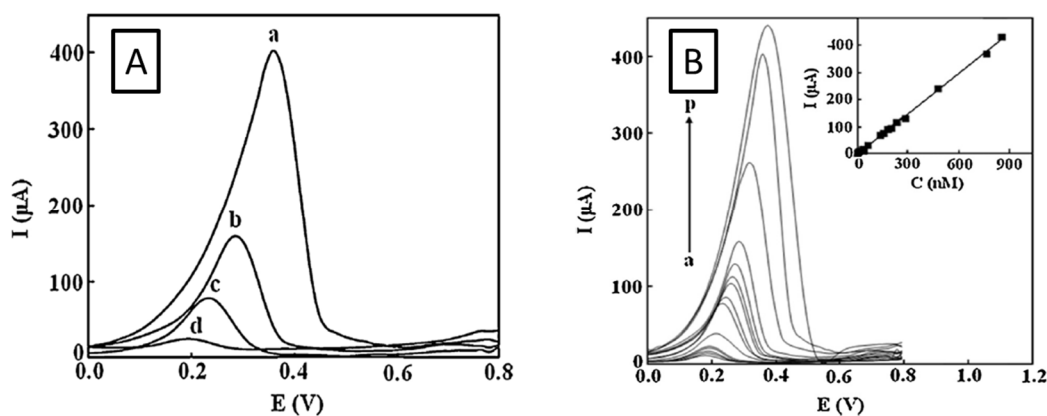


Fig. 8. A. Comparison of DPASV response of 7.5×10^{-7} M Ag(I) solution with IIP-CPE (a) ; NIP-CPE (b); plain CPE (c) and IIP-CPE without Ag(I) in accumulation medium. B. DPASV voltammograms of IIP-CPE for a concentration range between 2.8 nM and 850 nM (Reprinted by permission from Elsevier, Copyright 2014 [40])

4.3. Selectivity of modified sensors

When analysing trace amounts of metallic ions in real samples like environmental ones, it is essential to have a sensor presenting good selectivity properties. Indeed, such samples pose the problem that the target may be masked by interfering species. This is where the IIPs thanks to their intrinsic properties fully find their interest. To evaluate the selectivity performances of IPECS, different methods are implemented depending on the used electrochemical technique.

In the case of potentiometry, selectivity coefficients ($K_{A,B}$) can be measured taking into consideration the activities of the target ion A and of an interfering ion B. In the reviewed literature regarding IPECS used in potentiometry, two methods are employed to assess the selectivity of the electrodes: the Matched Potential Method (MPM) and the Separate Solution Method (SSM). The full description of MPM and SSM can be found in the IUPAC report on potentiometric selective coefficients of ISE [121]. Most authors using MPM to determine selectivity coefficients showcase very limited results with coefficients around 10^{-2} and 10^{-3} [78,80]. On the other hand, Shirzadmehr et al present an Hg(II)-imprinted carbon paste electrode with coefficients ranging from 7.40×10^{-4} to 3.50×10^{-6} [89]. However, as MPM is very outdated and has been abandoned in the field of ISE, future research regarding IPECS in potentiometry should acknowledge the development of the field in terms of selectivity coefficients to allow for an unbiased comparison with other ISEs [122–125]. Using the SSM method, Yolcu et al. also measured modest selectivity coefficients for their Cu(II) IPECS: $K_{Cu(II)/B}$ varied from $10^{-2.54}$ for Zn(II) to $10^{-4.98}$ for Li(I) [85]. Shamsipur et al. presents the most encouraging results with coefficients calculated with SSM around 10^{-4} and lower [40]. In any case, one criticism of most IPECS used in potentiometry is the use of IIP particles synthesized with commercial functional monomers or by the “trapping” procedure. One way to enhance the selectivity of these sensors would be to increase the selectivity of the IIP particles by optimizing the IIP synthesis.

When it comes to voltammetry, the selectivity of the sensors is usually evaluated through the determination of the limit of tolerance. This is defined as the maximum concentration of interfering ions that causes a relative error of around 5% in the analytical signal determination (with a classical reference value around 5%). As illustrated in Table 9, these concentrations are expressed in the form: XX-fold excess of the given interferent compared to the target ion. Thus, some authors show that their carbon paste IPECS reach performances where even 500-fold excess of some interferents does not affect the measurement of the target analyte [40,59,104].

Table 9. Selectivity (interferent results), limit of detection and linear range limits of some IIP-modified electrodes.

Target Ion	Method	Type of electrode	Interferents	LOD (mol/L)	Linear Range (mol/L)	Ref.
Cu(II)	DPASV	GCE: electropolymerization pyrrole + methyl red	No interference with 10-fold excess Ni(II), Co(II), Cd(II), Cr(III) Ba(II), Fe(III), Al(III), K(I), Na(I) ; Significant interferences of Pb(II), Hg(II), Ag(I)	6.50×10^{-9}	$1.00 \times 10^{-8} - 1.00 \times 10^{-3}$	[117]
Hg(II)	SWASV	GCE: electropolymerization mercaptobenzotriazole-capped SiO ₂ particles	Limit of Tolerance (7%) not reached for 100-fold excess of Cu(II), Cd(II), Zn(II) ; 50-fold excess Pb(II) ; 10-fold excess Ag(I)	1.00×10^{-10}	$1.00 \times 10^{-9} - 1.60 \times 10^{-7}$	[15]
Mn(II)	SWASV	GCE: Deposition of IIP Particles, MWCNT, Chitosan and ionic liquid	Limit of Tolerance (6%) not reached for 100-fold excess Co(II), Cu(II), Fe(II), Zn(II), Cr(III) ; 80-fold excess Cd(II), Al(III), Pb(II), Hg(II) ; 10-fold excess Ni(II)	1.50×10^{-7}	$2.00 \times 10^{-6} - 9.00 \times 10^{-6}$	[45]
Cd(II)	DPV	GCE: Deposition of Fe ₃ O ₄ @IIP particles	Limit of Tolerance (5%) not reached for 100-fold excess Zn(II), Cr(III), Pb(II), Ni(II), Ag(I), Hg(II), K(I) ; 20-fold excess Cu(II)	1.00×10^{-10}	$8.00 \times 10^{-9} - 8.00 \times 10^{-7}$	[72]
Cu(II)	DPASV	GCE: in-situ Crosslinking of chitosan with epichlorohydrin	Limit of Tolerance (7%) not reached for 10-fold excess of Al(III), Co(II), Cr(VI), Fe(II), K(I), Mg(II), Mn(II), Na(I), Ni(II), Zn(II), Pb(II), Cd(II)	1.50×10^{-7}	$5.00 \times 10^{-7} - 1.00 \times 10^{-4}$	[36]
Pb(II)	DPASV	CPE with IIP particles	No significant interference with 45-fold excess Cd(II), Mn(II) 30-fold excess Ni(II), Fe(II) 25-fold excess Co(II), Zn(II), Cr(III), Hg(II) 10-fold excess Cu(II), Ag(I)	1.00×10^{-10}	$3.00 \times 10^{-10} - 1.00 \times 10^{-9}$ and $1.00 \times 10^{-8} - 1.00 \times 10^{-6}$	[42]
Mo(VI)	DPASV	CPE with Fe ₃ O ₄ @SiO ₂ @IIP particles	Limit of Tolerance (5%) not reached for 1000-fold excess Na(I), Ca(II), K(I), Ba(II), Mg(II), Zn(II), Co(II), Ni(II), Al(III), Mn(II), Cu(II) ; 200-fold excess Pb(II) ; 20 fold excess W(VI)	4.17×10^{-10}	$2.08 \times 10^{-9} - 5.21 \times 10^{-6}$	[59]
Ag(I)	DPASV	CPE with IIP particles	Limit of Tolerance (5%) not reached for 500-fold excess Na(I), K(I), Mg(II), Ca(II), Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Pb(II), Hg(II), Al(III), Cr(III), Fe(III), Au(III)	9.00×10^{-10}	$2.80 \times 10^{-9} - 8.50 \times 10^{-7}$	[40]
Ce(III)	AdSV	CPE with IIP particles	Limit of Tolerance (5%) not reached for 500-fold excess Er(III), Yb(III), Gd(III), Dy(III), Ho(III), Eu(III), Nd(III), Pr(III), Tb(III)	1.50×10^{-7}	$1.00 \times 10^{-6} - 2.00 \times 10^{-4}$	[104]

To underline the gain in selectivity brought by the introduction of IIPs, some authors compare them to other types of electrodes. For instance, Alizadeh et al. compared their IIP-Carbon Paste electrode (IIP-CPE) for the detection of Pb(II) to several other types of voltammetric sensors in terms of linear range, limit of detection and limit of tolerance [102]. This study revealed that only a CPE modified with 1,4 bis(prop-2'-enyloxy)-9,10-anthraquinone and a bismuth/poly (*p*-aminobenzene sulfonic acid) film electrode were competitive with their IPECS in presence of Hg(II), Cd(II) and Fe(III) interfering ions. Nevertheless, none of them were selective enough towards Cu(II) which in most cases interferes with Pb(II) determination at concentrations lower than Pb(II). In a similar way, Chen et al. also compared their electrodes based on Ce(III)-IIP with other CPE from other studies. For their IIP-modified CPE, a 500-fold excess of other rare-earth ions can be used without interfering with the measurement (carried out with DPASV) [104]. On the other hand, a 50-fold or 10-fold excess of rare earth ions were enough to interfere with the measurement when using a cetyltrimethylammonium bromide-modified CPE or a dipyriddy-functionalized nanoporous silica gel-modified CPE.

These few examples underline the attractiveness of IPECS: they can reach excellent performances in terms of selectivity. This property makes them a type of sensor worth considering for samples with a complex matrix where interferents can cause a real problem.

4.4. Real sample applications

Because of their easy handling and high selectivity, IPECS are widely used to quantify metal ions in a large variety of samples going from liquid samples to solid ones. Table 10 gives an overview of the broad range of application domains. In order to validate their results, authors usually compare them to those obtained with a "reference" method like AAS or ICP-MS. The strength of IPECS is their ability to provide reliable results while minimizing the amount of preparation steps. As can be seen from Table 10, results are typically in accordance with those determined with the reference method.

In the case of water samples, the method is very simple to implement because it requires little to no treatment [56]. A large variety of water samples can be studied, presenting different kind of matrix effect such as river [52], sea [82], tap [55], well and industrial waters [41,89]. Usually, the water samples are simply filtered to remove eventual solid particles and the pH is adjusted with a buffer solution to reach the optimal value for the target adsorption by the IIP [70,89]. When the target ion quantity in the real water sample is very low and cannot be reached by the IPECS, as assessed by the reference method, the solutions are usually spiked with the target ion before the measurement in order to reach the linear range domain of the IPECS [55,64]. The aim of this operation is to prove that the metal ion determination in the real sample is not affected by a matrix effect of the sample.

For other types of samples, additional steps are usually required prior to the measurement. In the case of solid foodstuffs (vegetables [101], fish [89], rice [103,108], flour [103],...), the measurement is preceded by a digestion step usually with nitric acid [59,120], a mixture of nitric acid and hydrogen peroxide [89,101,103], or nitric acid and hydrochloric acid [108]. The samples are digested at high temperatures or at ambient temperature, depending on the authors. Finally, this treatment is followed by a filtration step and the adjustment of the pH solution.

In a similar way, solid biological samples such as hair or dental amalgams require a digestion with nitric acid [89] or nitric acid/perchloric acid mixture [43,94]. While some authors describe a similar digestion step for serum samples [90,95], normally the samples are simply deproteinated and filtrated as to obtain a protein-free matrix [110]. Bali-Prasad et al. knowingly skip these steps as to reduce inaccuracies related to these pretreatment steps and obtain satisfactory results (recoveries between 98.2 and 99.7%) [56]. Urine samples often require no pretreatment except filtration and adjustment of the pH.

Other types of samples such as pharmaceutical samples [56,80], cosmetics [42,69,81], fertilizer [35,68], catalyst samples [104,120], battery sample [35] have also been analysed and use a combination of the aforementioned pretreatment techniques before the measurement, mainly acid digestion, filtration and the pH adjustment.

Table 10. Real Sample Applications, comparison with same samples analysed with other methods.

Target Ion	Method used	Sample	Spiking	Reference method used	Result (reference method) (mol/L)	Result (IPECS) (mol/L)	Ref
Hg(II)	SWASV	River Water	-	ICP-MS	4.00×10^{-10}	4.60×10^{-10}	[52]
Cu(II)	Potentiometry	Tap Water	Spiking 1.01×10^{-5} M	ICP-MS	1.01×10^{-5}	1.04×10^{-5}	[55]
Ag(I)	DPASV	Well Water	Spiking 4.63×10^{-8} M	GF-AAS	4.69×10^{-8}	4.55×10^{-8}	[64]
Uranyl	Potentiometry	Sea Water	-	NAA (Neutron Activation Analysis)	6.0×10^{-9}	5.9×10^{-9}	[82]
Hg(II)	Potentiometry	Wastewater	-	CV-AAS	1.15×10^{-7}	1.11×10^{-7}	[89]
Pb(II)	DPASV	Fruit Juice	Spiking 9.7×10^{-9} M	-	-	9.2×10^{-9}	[71]
Hg(II)	Potentiometry	Tuna (Fish)	-	CV-AAS	47.44 (ng/g)	47.10 (ng/g)	[89]
Cd(II)	DPASV	Rice	Spiking 8.9×10^{-8} M	-	-	8.6×10^{-8}	[99]
Zn(II)	Potentiometry	Blood	-	AAS	6.39×10^{-6}	6.35×10^{-6}	[90]
Zn(II)	Potentiometry	Urine	-	AAS	6.24×10^{-6}	6.16×10^{-6}	[90]
Hg(II)	Potentiometry	Dental amalgam	-	CV-AAS	4.24×10^{-7}	4.11×10^{-7}	[89]
Cu(II)	DPASV	Hair	-	GF AAS	13.1 ($\mu\text{g/g}$)	13.4 ($\mu\text{g/g}$)	[43]
Uranyl	DPV	Soil	Spiking 2.0×10^{-8} M	ICP-MS	1.90×10^{-8}	1.70×10^{-8}	[60]
Ce(III)	DPASV	Catalyst	-	ICP-AES	1.50×10^{-5}	1.59×10^{-5}	[104]

5. Conclusions and perspectives

From the reviewed literature, it appears that IIPs show great promise as selective receptors to prepare different types of electrodes for IIP-modified electrochemical sensors. The flexibility of their preparation makes IIPs excellent candidates for the design of selective biomimetic electrochemical sensors, for which they could be in competition with bioreceptors such as peptides, enzymes and functional nucleic acids. Nevertheless, in comparison, IIPs present the advantage of being quite easy and inexpensive to prepare in different formats (particles or films) depending on the kind of desired electrode. Moreover, as IIPs are stable over time and in a large range of temperature and liquid media, including acidic and basic ones, they can provide sensors with a long lifespan suitable for applications in real and complex environments.

IIPs can be incorporated into IPECS in the form of particles (in carbon paste or membrane electrodes for example). One advantage of using IIP particles as additives is that they can first be fully characterized in this format in terms of binding capacities (through classical isotherms for instance), selectivity and imprinting effect. If necessary, their composition and synthesis conditions can be optimized prior to their incorporation in the IPECS. When they are used for voltammetric detection,

these IPECS have shown low LOD (down to a few pmol/L) and have proven extremely efficient when it comes to selectivity, allowing the electrodes to function at a 500-fold excess of interfering species. In the case of potentiometry, researchers were successful in fabricating ISE where traditional ionophores were replaced with IIP particles. While the results are not yet comparable to “classical” ISE, they can be encouraging to deepen this field of application. To further validate this proof of concept, it would be highly beneficial to compare the performances of a classical ISE with that of an IIP-based ISE that contains the same ionophore (either trapped or in the form of a functional monomer in the IIP).

On the other hand, it is also possible to fabricate IPECS by using IIPs in film format. This can be done by formation of the imprinted polymer directly on the electrode surface through the sol-gel technique or by electropolymerization for example. In that case, the characterization of the above-mentioned properties of the IIP can only be done by electrochemistry and surface characterization techniques. Nevertheless, growing IIP films on the surface of the electrode can favour the transfer of electrons from the bound metal ions to the electrode, and thus decrease the LOD. Although this route appears particularly appealing, there is still room for improvements using electropolymerizable crosslinkers for IIPs prepared by electropolymerization to stabilize the binding cavities. Another interesting route to be developed could be to prepare IIP films through a grafting and FRP procedure to covalently bind the IIP to the electrode surface.

Thanks to their remarkable properties, IPECS are excellent candidates to answer the growing demand for efficient tools to monitor metal ions *in situ*. However, an important effort is still required to incorporate them into portable analytical tools. This might be a challenging issue in the next few years.

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