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Ion-selective Electrodes (ISEs) for Cd^{2+}, Hg^{2+} and Pb^{2+}: Requirements for Correct Measurements and Application in Analysis of Potable, Industrial and Waste Waters

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Abstract: Ion-selective electrodes are widely used for non-destructive, rapid, sensitive and precise determination of many ions in a great variety of media and therefore provide a powerful analytic tool. If ISEs produced by Orion Research are universally recognized, other manufactured electrodes are cheaper and easy to supply; some electrodes can be prepared in the laboratory. These electrodes must be tested under well-defined criteria. Results scattering in the scientific study and variability of analytic conditions in each specific case, make it difficult the direct exploitation of the results accumulated by other researchers. So, a systematic survey of some ISEs to be applied later in water pollution checking is suggested. This study account for the more or less facility of use, the sensitivity limits, the interferences find and describe the titration procedures developed.

Key words: Cationic electrodes, analytical purposes, optimal cases, water mineral pollution

INTRODUCTION

Ion-selective Electrodes (ISEs) have been known for the past 3 decades. The main appeal of ISEs lies in the simplicity of the measuring technique and instrumentation and in their suitability for continuous monitoring, which makes them particularly useful in routine control analysis and pollution control. Moreover, during the last few years the scope of ion-selective electrodes has been extended to include trace determination of the species (Pretsch, 2007; Brown and Milton, 2005). Therefore, the analysis by ISEs is a preferred procedure for those ions for which selective electrodes are available.

However, to obtain meaningful results a number of conditions must be met, conditions which are sometimes contradictory and difficult to fulfil. A severe limitation is imposed on measurements with ISEs because of a fact inherent to most electrochemical methods: Namely, that the measurement depends on heterogeneous reactions occurring at the electrode-solution interface. Consequently, the reproducibility and long-term constancy of the conditions at the interface is of paramount importance for accurate and reproducible measurements. There is no general solution to this problem and an ideal state can be approached more or less closely only by judicious selection of the experimental conditions. So, ion-selective electrodes are to use carefully; appropriate methods, based on a good comprehension of the involved phenomena, must be looked for to obtain reliable and reproducible results.

The first part of the present study was devoted to the experimental determination of the principal characteristics of the lead, cadmium and mercury ISEs and the study of the most important parameters affecting electrode performance such as the pH, the ionic strength, the presence of interferents and the temperature. The achieved results were used to specify the titration procedures, which found practical application in the form of analysis of different water samples.

CHARACTERISTICS OF THE ISEs

Lead and Cadmium ISEs are from (Tacussel), while preparing an HgO electrode by decomposition at 45°C of $Hg\ (NO_3)_2$ on the surface of a titanium support (Ali-Mokhnache and Messadi, 1992).

The pH is readily measured with the glass electrode. The indicator electrodes are coupled with either the calomel or the silver chloride reference electrodes.

A direct reading Beckman pH-meter/ millivoltmeter, modelΦ 60, having a resolution of about 1 mV was employed.

The ionic strength of the solution which influences the activity coefficients of the species present was held

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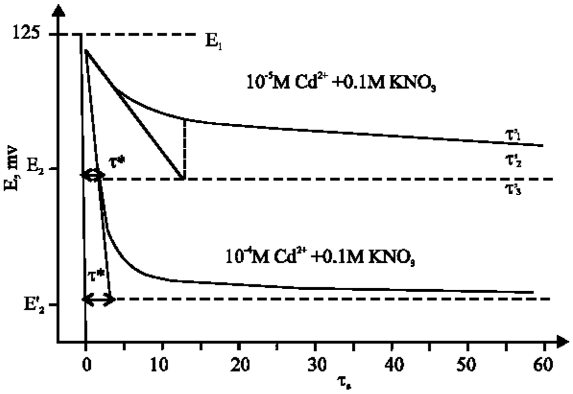

Fig. 1: Kinetics of establishment of the potential of electrode Cd^{2+} ions

constant by addition of KNO_3 (neutral electrolyte), which is justified by the weak value of the calculated selectivity coefficients. The optimal pH was adjusted by addition of pH buffers prepared according to Lourie (1979).

Reproducibility: It was charasterized by the standard deviation estimated (Cetama, 1969) starting from the relationship:

$$\text{Standard deviation} = \frac{1}{b_n}\left[\frac{(\sum Ei - E)^2}{n}\right]^{0.5} \qquad (1)$$

Valid for a number $n \leq 5$ of measurements of the potential; E_i is the ith measured potential and E the average potential; b_n depends on the number of measurements and is equal to 1.253 for n = 4.

Estimated standard deviations of the potential values, measured by the known addition method, are reproduced hereafter:

ISE	Pb^{2+}	Cd^{2+}	Hg^{2+}
standard deviation (mV)	0.54	0.89	0.63

They correspond, in the most unfavourable case, with the meter precision.

Response time: If an ISE is transferred from a solution with determined activity a_1 to a solution with a determined activity a_2, the E_{ISE} value does not change instantaneously from initial value E_1 to the value corresponding to activity a_2, E_2, but the time course of E_{ISE} is given by curve of a typical shape shown in Fig. 1.

Practical response time τ_{90} has been defined (IUPAC, 1994) as the time during which E changes from value E_1 to value E_1+0.9 (E_2-E_1), i.e. during which E_{ISE} changes by 90% of the total change from E_1 to E_2.

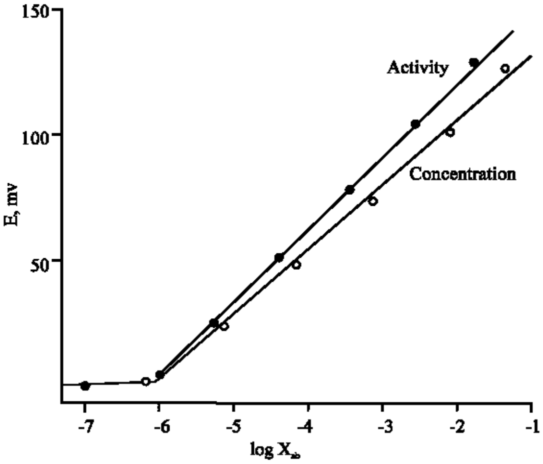

Fig. 2: Calibration curve for electrode PbX

The electrodes reach their equilibrium in less than 2 min for high concentrations, whereas slower responses (several minutes) are observed when one approaches the determination limits (10^{-6}-10^{-7} mol L^{-1}). This result is rather normal since in addition of the diffusion through the boundary layer, the dissolution of the membrane acquires a particular importance for the electrodes working under their determination limit conditions. The relaxation times (τ^*) are largely lower than 10 sec (Table 1).

Note that for a stirred solution the relaxation and response times are divided by 10. The effect of solution movement can be explained by a significant variation of the diffusion rate at the solid/liquid interface and through the boundary layer.

Effect of the test ion concentration/activity on the ISE potential: The ISE potential depends directly on the test ion activity and only indirectly on its concentration. In what follows, the test ion activity was calculated by multiplying its (known) concentration by the average activity coefficient taken from (Dobos, 1978).

Figure 2 shows the dependence of the ISE potential on the logarithm of the concentration/activity of Pb^{2+}ions.

Curves treatment by the average deviations method made it possible to determine the slopes of these lines (S_c; S_a) along with intercepts (E_c; E_a). The value of these parameters, as well as the theoretical slopes (S_t), are displayed on Table I which also emphasizes the dynamic linear range and the lower practical determination limit.

Influence of the ionic strength: Table 2 shows that Pb^{2+} ion activity coefficients and thence the measured electrode potential (E_1), vary in the opposite direction of the ionic strength, under constant concentration of the Pb^{2+} ions.

Table 1: Some results deduced from the studied ISEs

ISE/solution	pH	E^0_c(mv)	E_a(mv)	S_c	S_a	S_t	Linear range	Limit (mol.L^{-1})
$Pb^{2+}/Pb(No_3)_2$	4.7	159	167	26.1	28.8	29.8	$10^{-\circ}10^{-6\,(*)}$	$10^{-7\,(*)}$
$Cd^{2+}/Cd(No_3)_2$	4.7	-	-	28.0	29.0	29.8	$10^{-\circ}10^{-5\,(*)}$	$10^{-7\,(*)}$
$Hg^{2+}/Hg(No_3)_2$	-	-	-	-	-	-	$10^{-\circ}10^{-8}$	10^{-8}

(*) Values somewhat different of those announced by the constructor

Table 2 : Effect of the ionic strength I, adjusted by addition of KNO_3, on the $^{2+}$ *ISE potential for a constant concentration (*10^3 *mol. L*$^{-1}$*) in* $^{2+}$ions

I	4×10^{-3}	1.3×10^{-2}	1.03×10^{-1}	1×10^{0}
E_1 (mV)	77	73	69	65
$\gamma\pm$	0.88	0.69	0.40	0.15
a_i	0.88×10^{-3}	0.69×10^{-3}	0.40×10^{-3}	0.14×10^{-3}
E_2 (mV)	73	67	57	51

Note that E_1 is superior to the E_2 electrode potential calculated for Nernstian behaviour by using the values of the activities assembled in Table 2; the difference is so much important as the ionic strength is high. This apparent discrepancy has its origin in the omission of the interference K^+ ions which concentration increases with the ionic strength. Indeed, the Pb^{2+} ISE potential in the presence of the K^+ ions is given by the equation :

$$E\ E^0+\frac{s}{n}\log\left[a_{(Pb^{2+})}+K_{(Pb^{2+}/K^+)}\times a(K^+)\right] \tag{2}$$

Where:

$$K_{(Pb^{2+}/K^+)}$$

is the selectivity coefficient, which shows that the antagonistic evolution of the activities of lead and potassium moderates the diminution of E.

Temperature effect: The solutions being thermostatted within ±0.1 °C, negligible temperature effect was observed when the ion-selective/reference electrodes are maintained at the same constant temperature.

It is recommended that the measurement be carried out at a somewhat elevated temperature (At 25-30°C), as the electrode response is faster and precision of measurement is improved.

Influence of the PH: The solution pH affects the function of all ISEs , either through interference of hydroxonium or hydroxyde ions in the membrane reaction, or through chemical interference in solution, or both.

Moreover, the pH value can affect the equilibria of the interferents in the solution. The pH must thus be adjusted with all these effects in mind. Fortunately, it is usually sufficient to maintain the pH within a certain region rather than a single precise value.

Figure 3 shows the effect of the pH on the potential of the Pb^{2+} and Cd^{2+} ISEs soaked in various solutions.

In the range of pH: From 3.6-9.0, the pH of the Cd^{2+} solution affects little the CdX electrode potential. The potential increase with pH<3 is not surprising if one takes into account the exchange reaction between the membrane of the electrode and the H^+ ions which concentration increases in this region of pH.

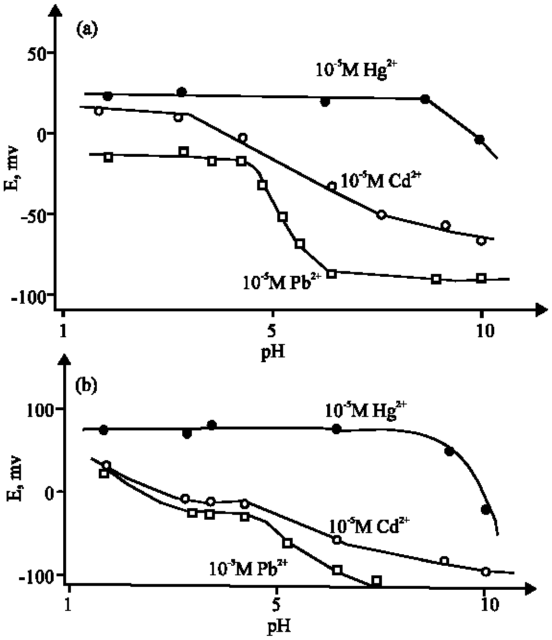

Fig. 3: Influence pH on the potential of the electrodes CdX (A) and PbX (B) plunged in various solutions

For the Hg^{2+} solution, the potential of the electrodes HgO, CdX and PbX remains constant in the region of pH: from 1.6-9.0. The potential decrease with pH > 9.5 is caused by the formation of $Hg(OH)_2$.

Practically, 2 regions of pH make it possible to carry out measurements with an acceptable error level: from 3.5-5.0 (Pb^{2+}, Cd^{2+}) and from 6.0-8.0 Hg^{2+}.

It must be noted that a judicious choice of the solution pH makes it possible to shorten the extent of interferences of the ferrous and ferric ions present in all water. Moreover, for a pH of about 1.7, the PbX and CdX electrodes can be used for analytical determination of the Fe^{3+} ions present for concentrations higher or equal to 10^{-5} mol.L^{-1}.

Interferent ions: Our results show that, under the conditions of measurement (V = 50 mL solution: X^{n-} (10^{-3} M) + 5 mL KNO_3 (1M); pH= 4.7) some of the following anions : F^-, Cl^-, Br^-, I^-,CNS^-, ClO^-_3, ClO^-_4, NO^-_3, $S_2O_3^{2-}$, Cro_4^{-2}, NO_3^-, $S_2O_3^{2-}$, CrO_4^{2-}, SO_4^{2-}, CO_3^{2-}, $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$, can have a great influence on the electrode potential.

HgO : Br^-, $S_2O_3^{2-}$, $CrO^{2-}{}_4{}^{2+}$, $[Fe(CN)_6]^{4-}$
CdX: I^-, $[Fe(CN)_6]^{3-}$
PbX: CrO_4^{2-}, CrO_3^{2-}, $[Fe(CN)_6]^{3-}$

It is thus possible to apply the anions F^-, Cl^-, I^-, CNS^-, ClO^-_3, ClO^-_4, NO^-_3 and $S_2O_4^{2-}$, to mask the cations being able to intervene in the working of the electrode.

Among the studied cations Ag^+, Na^+, Ca^{2+}, Hg^{2+}, Cd^{2+}, Fe^{2+}, Mn^{2+}, Zn^{2+}, Cr^{3+}, Fe^{3+}, Al^{3+}, a marked influence of the Fe^{3+} and Mn^{2+} on the potential of HgO electrode was noticed (Fig. 4), whereas the CdX and PbX electrodes undergo especially that of the cations Fe^{2+}, Fe^{3+} and Hg^{2+}.

Thus, for example, the Fe^{3+} ions can be masked by formation of $[FeF_4]^-$ (constant stability : $10^{16.1}$) and the Hg^{2+} ions precipitated in the form of Hg_2Cl_2 (solubility product: 1.1×10^{-18}) by addition of Cl^- ions ; excess of F^- or Cl^- employed do not affect the electrode potential.

Selectivity: The ISEs never have a perfect selectivity; it is thus essential to make sure, before any ionic measurement, that the examined solutions do not contain interferent ions.

The causes of interferences are generally related to the presence of ions which intervene in the process of ionic exchange at the interface. Nikolsky established a relationship between the potential of an pH measuring electrode and the activities of H^+ and interferent ions; this relation was then generalized with whole ISEs (Pungor, 1992), in the form (3) which is a modified form of the equation of Nernst :

$$E = E_0 + \left(\frac{RT}{z_i F}\right) \mathrm{Log} \left[\begin{array}{l} a_i + K_{i,j} \left(a_j\right)^{z_i/z_j} \\ + K_{i,k} \left(a_k\right)^{z_i/z_k} + ... \end{array} \right] \quad (3)$$

Where, the ions j, k ... of charge numbers z_j, z_k..., presenting a_j, a_j activities interfere with the measure of ions I of charge number z_i: and activity a_i.The coefficients K_{ij}, $K_{ik...}$ are the selectivity coefficients of the ISE for ion i with respect to ions j, k…

The selectivity coefficient is frequently a function of the composition of the analyte; nonetheless, it provides an indication of the effect of interfering ions on the determination of the test ion.

In this research the mixed solution technique (IUPAC, 2000) was used for the determination of selectivity coefficients. The emf of a cell consisting of an ISE and a reference electrode is measured at a constant interference activity a_j and variable determinand activity a_i .The emf values are plotted against the logarithm of the determinand activity. The intercept of the asymptotes to this curve gives the a_i value that is used for the calculation of $K_{i,j}$ from the relationship:

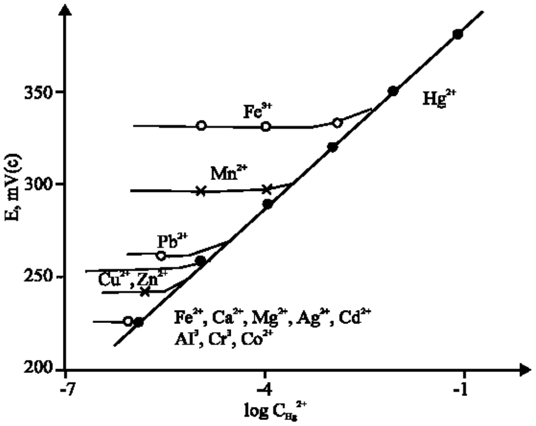

Fig. 4: Influence of concentration and nature of ions on the potential of the electrode specifictoions Hg^{2+}

Table 3: Coefficients of K_{ij} selectivity of the electrodes designed for ions I compared to the interfering ion J. Solutions of ion I of concentrations 10^{-6}-10^{-1} mol L^{-1}; solutions of ion I of same concentrations in the presence of the ion J with a constant concentration 10^{-3} mol L^{-1}

j	$K_{Pb^{2+}/j}$	$K_{Cd^{2+}/j}$	$K_{Hg^{2+}/j}$
Zn^{2+}	6.8×10^{-3}	7.3×10^{-2}	4.6×10^{-3}
Cu^{2+}	1.0	10	6.8×10^{-3}
Fe^{2+}	0.21	39.8	10^{-2}
Co^{2+}	10^{-2}	2.7×10^{-2}	0.14
Ca^{2+}	6.8×10^{-3}	7.35×10^{-2}	3.16×10^{-3}
Mg^{2+}	10^{-2}	1.84×10^{-2}	2.15×10^{-3}
Hg^{2+}	100	100	1.0
Cd^{2+}	3.1×10^{-3}	1.0	1.46×10^{-3}
Na^{+}	10^{-2}	2.5×10^{-2}	2.15×10^{-3}
Ag^{+}	10^{-2}	5.0×10^{-2}	2.15×10^{-3}
Fe^{3+}	2.8×10^{-2}	7.9	2.15
Al^{3+}	10^{-2}	5.4×10^{-2}	6.8×10^{-4}
Cr^{3+}	10^{-2}	1.3×10^{-2}	1.4×10^{-6}

$$K_{i,j} = \frac{a_i}{a_j^{z_i/z_j}} \qquad (4).$$

The values of the selectivity coefficients are collected in Table 3.

It can be seen that the Pb^{2+} ISE has a great selectivity for the Pb^{2+} ions in the presence of the ions Zn^{2+} and Cr^{2+}. The ions Hg^{2+}, Cu^{2+} and Fe^{3+} can intervene in the detection of the Pb^{2+} ions.

For the CdX electrode the titrating of the Cd^{2+} ions is possible in the presence of the ions Zn^{2+} and Cr^{3+}. The

Table 4: Acceptable maximum ratio of concentrations [interferent ions (j)/determinand ions (I)]

ISE	Interferent ions j				
	Concentration ratio of ions j/i				
$1:10^4$	$1:10^3$	$1:10^2$	1:10	1:1	10:1
Pb^{2+}, Hg^{2+}		Fe^{2+}; Fe^{+3} Cu^{2+}	Ag^{2+}; Co^{2+}; Mg^{2+}; Al^{+3}; Cr+2	Ca^{2+}; Mn^{2+} Zn^{2+}, Cd^{2+}	
Cd^{2+}, Hg	Fe^{2+}; Fe^{+3}		Ag^+; Ca^{2+}; Mg^{2+}; Zn^{2+}; Ci^{2+}	Al^{3+}; Cr^{3+}	
Hg^{2+}	Fe^{+3}		Fe^{2+}	Ag^+; Cu^{2+};$Pb^{2+}Co^{2+}$	Al^{3+}; Cr^{3+}

ions Fe^{3+}, Hg^{2+} and Cu^{2+} have a great influence on the potential electrode in the presence of the Cd^{2+} ions.

The HgO electrode is sensitive to the Hg^{2+} ions in the presence of the various ions except for Fe^{3+}.

The prevision of the selectivity of an electrode, starting from some preliminary data, is important.To carry out such an objective we used the simplex method (Hazourli, 1998). It consists in optimizing a linear function of several variables subjected to a set of linear constraints too, which limit the interval of calculation and thus make it possible to accelerate the convergence of the iterative process.

The application of this method leads to the same values determined previously within 5×10^{-7} in the most unfavourable case. The iteration count depends on nature of the ion pairs considered and the value adopted to initialize calculations.

Moreover, our experimental results allow to determine the acceptable maximum ratio (interferent ions/determinand ion), in fixing to 1% the error due to the influence of interferent ions (Table 4).

ANALYSIS OF VARIOUS WATERS

Analysis procedures of the Pd^{2+}, Cd^{2+}, Hg^{2+}

Titration of the Pb^{2+} ions: To 50 mL of the sample one adds 5 mL of pH (= 4.8) buffer solution. The F^{3+} ions are masked using a 0.1 $mol.L^{-1}$ NaF solution (1-10 mL); the ions Fe^- forming with the Fe^{3+} ions a rather stable complex. The Hg^{2+} ions (with concentration lower than 10^{-6} mol L^{-1}) are precipited by addition of 1 mL of a 10^{-4} mol L^{-1} NaCI solution (formation of scarcely soluble Hg_2CI_2)

Formation of Pb_2CI_2 in the presence of weak concentrations of ions CI^-, does not take place because of a great enough value of $PbCl_2$ solubility product. Solubility is equal to 3.9×10^{-2} mol L^{-1}, whereas that of Hg_2Cl_2 is 6.5×10^{-7} mol L^{-1}. The ions CI^- do not influence the potential of the PbX electrode.

Anions CO^{2-}_3, $[Fe(CN)_6]^{3-}$, CrO^{2-}_4, Iw^- being able to intervene in the measurement of the potential it is necessary, before titrating the Pb^{2+} ions, to make sure their presence in the sample to analyze and mask them if required.

The CrO^{2-}_4 ions can be masked by employing 1mL of a 0.1 mol L^{-1} $BaCl_2$ solution. The ions $[Fe(CN)_6]$ ^{3}are converted into $[Fe(CN)_6]^{4-}$ by adding 1 mL of 0.1 $mol.L^{-1}$ $S_2O_3^{2-}$ solution (reducing agent not influencing the potential measurement).The presence of ions I^- and CO_3^{2-} simultaneously with that of the Pb^{2+} ions is not very probable, because it would be formed scarcely soluble compounds such $PbCrO_4$ (1.7×10^{-14}) or PbI^{2+} (8.9×10^{-9}).

Titration of the Cd^{2+} ions: To 50 mL of the sample one adds 5mL of pH (= 4.8) buffer solution. The influence of the ions Fe^{3+}, Hg^{2+}, CrO_4^{2-};$[Fe(CN)_6]^{3-}$ can be eliminated while operating like previously, whereas the elimination of that of Pb^{2+} is obtained by addition of 1mL of 0.1 $mol.L^{-1}$ $^{2+}$ solution (formation of scarcely soluble $PbSO_4$).

The Cu^{2+} ions are eliminated by operating a cathodic pre-electrolysis of the sample at constant potential. The electrode potential is selected according to the curve I = f (E) in the region where there is the only reaction:

$$Cu^{2+} + 2e^- \longrightarrow Cu$$

Note that the reduction of the $^{2+}$ ions occurs in a potential region more negative than for the Cu^{2+} ions.

Titration of the $^{2+}$ ions: To 50 mL of the sample one adds 5 mL of pH (= 6.86) buffer solution .In this region of pH the interfering ions Ag^{2+}, Pb^{2+}, Cd^{2+} and Fe^{3+} give scarcely soluble hydroxydes, whereas the influence of Fe^{2+}, Ni^{2+}, Zn^{2+} and Co^{2+} is negligible.

One can control the concentration of Hg^{2+} with the HgO electrode or with PbX and CdX electrodes which have high selectivity coefficients and

$$K_{Pb^{2+}/Hg^{2+}} \text{ and } K_{Cd^{2+}/Hg^{2+}} \text{ (nearly 100).}$$

Application: The practical application of the electrodes was in the analysis of potable industrial and waste waters. Table 5 displays the obtained results.

One can note the concentrations rather large in Cd^{2+} of samples II.3 and III.4 and in Pb^{2+} for samples III.3 and III.4. The concentrations in Hg^{2+} are lower than 2×10^{-4} mg L^{-1}, except for samples II.1 and III.2, which can be due

Table 5: Recapitulative results of the cations determination in potable (I), industrial (II) and waste (III) waters, by direct ionometry and potentiometric titration

Samples		Pb^{2+}(mg L^{-1})	Cd^{2+}(mg L^{-1})	Hg^{2+}(mg L^{-1})
I	1-Annaba city	$\langle 2\times10^{-2}$	$\langle 1.6\times10^{-3}$	$\langle 2\times10^{-4}$
	2-Algiers city	$\langle 2\times10^{-3}$	$\langle 1.6\times10^{-2}$	$\langle 2\times10^{-3}$
	3-Oran city	$\langle 2\times10^{-2}$	$\langle 1.6\times10^{-3}$	$\langle 2\times10^{-4}$
II	1-Iron and steel plant before treatment	-	$\langle 1.6\times10^{-2}$	$\langle 2\times10^{-3}$
	2-Iron and steel plant after treatment	$\sim 4\times10^{-2}$	$\langle 1.6\times10^{-3}$	$\langle 2\times10^{-4}$
	3- Mechanical plant	$\langle 2\times10^{-3}$	0.9^{*}	$\langle 2\times10^{-4}$
III	1-Iron and steel plant	$\langle 2\times10^{-3}$	$\langle 1.6\times10^{-3}$	$\langle 2\times10^{-4}$
	2-Chemical plant	0.18^{*}	$\langle 1.6\times10^{-3}$	$\sim 2\times10^{-3}$
	3-Electrochemical plant	2.2^{*}	0.16^{*}	$\langle 2\times10^{-4}$
	4-Mechanical plant	$\langle 2\times10^{-2}$	0.9^{*}	$\langle 2\times10^{-4}$

to the weak influence of the ions Pb^{2+} and Cd^{2+} in the used pH interval.

We confirmed by traditional polarography the results obtained for sample III.3. We thus displayed the presence of the cations Zn^{2+} (concentration close to that of the Cd^{2+} cations) and Cu^{2+} (0.85 mg L^{-1}).

CONCLUSION

Measurements with ion-selective electrodes appears at first sight extremely simple.

However, to obtain meaningful results a judicious selection of the experimental conditions is necessary. We tested ISEs for Cd^{2+}, Pb^{2+} (from Tacussel; France) and Hg^{2+} (prepared in the laboratory). The principal characteristics of these electrodes were determined experimentally and some physical and chemical parameters were studied too. We checked the reproducibility of the measured potentials and determined practical detection limits and dynamic linear ranges (which differ from those announced by manufacturer). The thresholds of sensitivity make it possible, for the cations studied, to meet the requirements of the standards. The presence in the solution of ions others than that of interest (especially those of the same sign) often limit the use of the selective electrodes. The coefficient of selectivity can provide a suitable indication for the extent of the possible interference. The coefficients of selectivity computed by the Simplex method reproduce those given in experiments. The interest of this model lies in the fact that it offers the possibility of predicting the extent of the interference. The practical application of the electrodes was carried out by controlling potable, industrial and waste water samples.

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