APPLICATION OF ION—SELECTIVE ELECTRODES TO METAL FINISHING INDUSTRIES

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(presented at the Conf. Industrial Metal Finishing, Bangalore, Oct 1976)

Although a number of practical procedures involving ion selective electrodes (ISS) have been suggested in the place of the classical analytical methods, these have not yet gained popularity Considering the various advantages offered by ISE's such as the ease of analysis of coloured and turbid solutions, covering a wide range of concentrations with the same precision, fast response, results independent of the volume or weight of sample, minimum or no pretreatment of samples and adaptability to on-line analysis these electrodes offer a simple solution to analysis of the industrial samples. A brief description of electrodes available followed by the analytical methods is presented in the review.

A proper control of the constituents of the baths used in electroplating and metal finishing is a pre-requisite for good results. This demands frequent analysis of such baths. The conventional methods of analysis have limitations of their own, e.g. difficulties are encountered with coloured and turbid solutions in titrimetry and pretreatment of the sample has invariably to be done in colorimetric method. Also these methods are time consuming and, in no case, can be used for on-line analysis. Of late a variety of instrumental and electroanalytical techniques are finding their way in the metal finishing industries specially because stringent specifications are prescribed for control and discharge of effluents [1]. The ion-selective electrodes (ISE) which are classified under electroanalytical techniques, can be used in the analysis of electroplating and metal finishing baths and effluents. ISEs can be used for analysis of electrodeposits also.

The major advantages of using ISEs for analysis are [2,3] (1) their ability to cover a large range of concentrations with the same precision, (2) their fast response to concentration changes. (3) requirement of little or no pretreatment of samples, (4) possibility of analysing coloured and turbid solutions, (5) independence of results with respect to volume and weight of the samples and (6) their comparative cheapness. Also in many cases, on-line analysis is possible. In some cases where ISEs are amenable to interferences from other ions, the interferences can be avoided by simple pretreatments of the samples. The ISE measures activity rather than concentration of ion in solution. However, by keeping the ionic strength of the background constant, the concentrations can be measured directly. The precision of the measurements by ISEs is about $\pm 2\%$ for monovalent and $\pm 4\%$ for divalent ions [2,4], which is well within the requirement of metal finishing industry.

It is surprising that although the ISEs can be used with a greater advantage in metal finishing industries, very few papers have appeared wherein they have been used in analysis of baths and/or effluents of these industries. Even recent reviews[4-9] on analytical methods for analysis of plating baths do not pay adequate attention to the use of ISE. This indicates that ISEs are yet to gain popularity in metal-finishing industries. The objective of this paper is to highlight the potentialities of ISEs in metal-finishing industries.

The ion selective electrodes essentially consist of an ion exchange membrane which develops a potential when in contact with a solution of the ion of interest. The magnitude of the potential is proportional to the concentration of the ion in solution. The glass pH electrode is a typical example of ISE which senses the hydrogen ions in solution. Similarly electrodes sensitive to cations like Cu (II), Ag (I), Pb (II) etc. and anions like Cl^-, CN^-, S^{2-} etc. have been developed. The electrodes may be classified in three categories based on the nature of the sensing membrane, viz. solid membrane, liquid membrane and natural sequestering (neutral carrier) membranes. The third category of electrodes find their use mainly in biochemical analysis and are not of much relevance to metal finishing industry. Hence we will restrict our discussions in this article to the first two types of electrodes only. The solid membrane electrodes may further be classified into (1) homogeneous and (2) heterogeneous membrane electrodes.

The homogeneous membranes are prepared by high pressure compression of an insoluble salt of the ion of interest. The conductivity of the membrane is improved by incorporating Ag_2S or Ag_2Se or silver telluride along with the insoluble salt. The heterogeneous membranes are prepared by dispersing the active material (along with a conductance increasing

material, if need be) into a non-interacting (chemically neutral) base like siliconerubber, polythene, PVC etc.

The liquid membranes consist of a solvent (immiscible with sample phase) containing an appreciable concentration of an ionizable compound (containing ions to be sensed), preferentially soluble in the membrane phase. For carrying out the measurements the membrane is interposed between the sample solution and a standard solution of constant activity of the ions being sensed. The potential across the membrane is measured using reference electrodes dipped in standard and sample solutions.

The equipmets required for the measurements involving ISE are a high impedance, sensitive millivoltmeter and a reference electrode. One can use an expanded scale pH/milli-voltmeter or a digital pH/millivolt meter For routine work a sensitivity of ± 0.5 mV will be sufficient but for precision measurements, higher sensitivity (± 0.1 mV) will be required.

Concentration measurements using ISEs employ one of the following methods involving either (1) Direct calibration method (2) standard addition and standard subtraction methods or (3) titrimetric methods.

Direct Calibration Method :

The ISE is dipped into the sample solution which is under continuous stirring and the potential of the ISE is measured against a suitable reference electrode. The concentration of the sample is read from a calibration curve prepared by plotting potentials of known-concentration sample on a semilog paper. The ionic strength of both the sample as well as standard should be of same order.

Standard Addition and standard subtraction methods.

In standard addition [10,11] methods, to a known volume of the sample, known amount of standard solution of ion of interest is added and the difference in potential of the ISE is measured. The concentration of ion in sample can be either calculated or read off from standard addition tables [10]. The standard subtraction [10,11] method is reverse of standard addition method. The potential of ISE in known volume of sample is measured whereafter a known amount of standard solution which will react with the ion of interest in sample is added. From the change in the potential, the concentration of the ion of interest in sample is either calculated or read off from standard subtraction tables.

The main advantage of standard addition and subtraction methods is that exact ionic strength of sample and the amount of complexing agent need not be known provided it is in great excess. The standard subtraction method is of great use in case of ions for which no sensing electrode is available. While using standard subtraction method, care is taken not to add too large an amount of standard solution: otherwise all the ions being sensed by ISE will be consumed.

Titrimetric Method :

In this method, the IES serves as an indicator electrode in potentiometric titrations. Titrations are adopted when a high degree of precision is desired as also for indirect measurement of concentration of some ions for which no electrode is available. The titration procedure can be made simple if Granplot technique is used [2,12].

Constituents of plating and metal-finishing baths (both major and minor) and those present in effluents can be analysed using ISEs. In what follows, we describe such applications which are reported in literature, together with suggestive applications, some of which are currently being worked out in our laboratories. The applications are based on the use of solid membrane electrodes unless stated otherwise.

ANALYSIS OF CATIONS

Aluminium : Estimation of aluminium in anodizing baths has been suggested by Toblas[9] based on the reported methods for aluminium assay using a F^- ISE employing a titration procedure [13-15].

Cadmium : The availability of a cadmium ISE makes possible the monitoring of Cd^{2+} ion in non-cyanide baths directly.

In cyanide baths, cadmium ion concentration is determined by known addition method using a Cd(II) ISE after destroying the CN^- with excess hypochlorite, at pH 10. Concentration of Cd (II) upto 0.01 ppm can be detected[2].

Chromium : Chromium (+6) in plating baths can be measured with a perchlorate ISE. The sample is diluted (≈ 100 times) with 1M acetic acid before measurements[2].

Cr^{6+} may also be estimated using I^- ISE. After acidifying the sample with H_2SO_4, excess of known amount of KI is added and using known subtraction method, the Cr^{+6} concentration is determined[10].

Cr^{+6} in anodizing baths also can be monitored using the above method.

Since Cr^{+6} is toxic, it has to be destroyed and brought to the level of <1 ppm before effluents are disposed off. Monitoring can be done either automatically [1] using ORP (redox-probe) or manually by measuring Cr^{+6} concentration by any of the methods described already.

A Cr (III) ISE [16] has also been reported in literature and appears to offer possibility of estimating Cr(III) in metal finishing baths.

Cobalt: Estimation of Co(II) in plating solutions may be done by Chelometric indicator titrations with EDTA after adding Cu-EDTA indicator using a Cu(II) ISE [10]. The titration is done at pH 10. A cobaltous sensing electrode is reported in literature [17].

Copper: Copper in etching and acid plating baths can be estimated[2] using a Cu(II) ISE upto 6 ppb. Copper in pyrophosphate baths can be determined using a Cu (II) ISE either by known addition method after addition of excess of pyrophosphate or by titration with EDTA [10].

Monitoring of copper in effluents is essential as it is toxic. This may be done directly using a Cu (II) ISE.

Gold: Gold in cyande bath can be determined by titration with $AgNO_3$ using a Ag ISE [2]. The difference between free and total cyanide gives concentration of gold.

An indirect metood for estimation of gold in metal solutions in the pH range 1.2—2.3 using a I^- ISE is also available [18]. This method can be used only when I^-, Ag and mercury are not present in solution. The detection range of gold by this method is 10^{-6} M to 10^{-8} M.

Iron: Apart from the conventional method of estimating iron (II) by permanganate, iron can be easily determined by titrating with sodium iodate or sodium thiosulphate using a redox electrode [10].

Development of Fe (III) ISEs has also been reported [19,20].

Lead: Concentration of lead in plating baths can be determined by titration with sodium molybdate or sodium tungstate using a lead sensitive electrode[2]. Indirect titration with TEPA using a Cu(II) ISE has also been suggested for estimation of lead [21].

Manganese: Manganese estimation has been done by titrating with EDTA after addition of Cu-EDTA indicator to the sample. A Cu (II) ISE was used [10].

An electrode sensitve to manganese ions in solution has also been reported [22].

Molybdenum: Liquid membrane molybdenum ISE has been described in literature [23]. If Fe, V, W, Nb or Re are present in the sample, they should be either separated or masked before measurements as they interfere.

Indirect determination of molybdenum can also be done using a I^-sensitive electrode after addition of KI, H_2SO_4 and H_2O_2 in the sample [24].

Nickel: For determination of Ni (II) concentration, titration with EDTA[25] or TEPA[21] using a Cu (II) sensitive electrode is reported. This principle has been utilised for automatic monitoring of nickel in high speed nickel bath [2]. A Ni (II) sensitive electrode has also been reported in literature[26].

Silver: Silver in cyanide plating baths is determined by known addition method after adding $KAg(CN)_2$ complex. A Ag^+ISE is used[2,27]. Silver in non-cyanide baths can be estimated by using the Ag^+ ISE by direct calibration procedure.

Tin: The conventional redox titration of the sample with ceric sulphate is used to determine tin concentration in solution[10] as no ISE for tin as yet has been developed.

Tungsten: Concentration of tungsten in solution can be determined using an I^-ISE after addition of KI, H_2SO_4 and H_2O_2 to the sample [24].

Zinc: Zinc concentration can be determined with a Cu (II) ISE by titration of the sample with TEPA using a Cu-TEPA complex as indicator [21].

Zinc ion sensing electrodes have also been reported in literature [28] which may be useful in direct monitoring of zinc.

ANALYSIS OF ANIONS

Bromide: Determination of Br^-in nickel sulfamate bath using Br^-electrode has been suggested by Frant [2].

Chloride: Chloride in cyanide copper bath is estimated by titration with $AgNO_3$ using a Ag^+ISE [2].

In acid copper bath, chloride can be determined by known method using a Cl^-ISE [2]. Chloride in a variety of other baths can be determined using Cl^- sensitive electrode if $S^{-2}(<10^{-7}M)$, Br^-, $I^-$and $CN^-$are not present in significant amounts [10].

Chromate: Chomate is measured directly using a perchlorate liquid membrane electrode[2].

Development of a CrO_4^{2-} sensitive electrode has been reported in literature [29].

Cyanide: Cyanide in copper and brass plating baths is determined using a CN^-ISE after removal of Cu^{++} and Zn^{++} ions from solution by passing through a column of ion exchange[2].

In cadmium and zinc plating baths, $CN^-$is measured directly using a CN^-ISE after dilution of the sample with NaOH [2].

In silver plating baths, cyanide is determined by known addition method using a CN^-sensitive electrode [2,27].

Cyanide in gold plating baths is determined by titration with $AgNO_3$ using a Ag^+sensitive electrode after dilution of the sample with NaOH[2].

Cyanide in effluent has to be brought to a very low level before disposal. The sensitivity of CN−ISE is not sufficient for this purpose. Hence it is estimated using a Ag^+ ISE after treatment with acid and EDTA and adding K Ag $(CN)_2$ indicator at pH 11[30,31].

An alternate method for monitoring CN−is as follows. CN^-in effluents is destroyed by alkali chlorination or with hypochlorites. To make sure that all the CN^- has been destroyed, a slight excess of chlorine is added. The monitoring of Cl_2 is done by standard sub traction method using an I^- ISE [2]. An assembly for continuous monitoring of Cl_2 (cyanide) using above method has been reported in literature [2].

Fluoride: Fluoride in chromium plating baths can be estimated using a F^-ISE after diluting the sample with water and 0.13 M EDTA. The pH is adjusted to 9 by NaOH[32].

In chromating [33] as well as in pickling baths[34] F^-ion concentration can be determined directly with a F^-ISE.

Fluoride monitoring in waste water also can be done directly using a F^-ISE after adjusting the ionic strength [10].

Fluoborate: Estimation of fluoborate in plating baths is done using a fluoborate liquid membrane ISE[2]

Nitirate: Nitrate in pickling baths can be monitored using a NO_3^-liquid membrane ISE after diluting the sample [10].

In waste water and effluents No_3^-can be measured upto 10 ppm by a NO_3^-ISE If Cl^-ion concentration is significant, Ag_2SO_4 is added prior to measurements [10]. Alternatively, NO_3^-can be estimated after reduction with Devarda's alloy to NH_3 and sensing it with a NH_3 sensing probe. This is more sensitive method than previous one [35,36] upto 0.1 ppm).

Perchlorate: Perchlorate ion estimation in electropolishing solution can be done using a perchlorate liquid membrane ISE.

Phosphate: Po_4^{-3} ion in phosphoric acid polishing baths and in phosphating baths can be estimated using a F^-ISE and Gran's plot technique. An excess of known amount of lanthanum nitrate is added to the sample and excess of lanthanum is titrated with NaF using a F^-ISE[10].

Liquid membrane electrodes sensitive to PO_4^{-3} ion are also reported in the literature [37,38].

Pyrophosphate: Pyrophosphate estimation in baths can also be done using a F^-ISE by the method described for PO_4^{3-}estimation. However before adding lanthanum fluoride, sample is added to a hot solution of neutral sodium perchlorate and cooled [10].

Sulphate: Sulphate in Watts nickel bath is estimated by known subtraction method with a lead sensitive electrode. Sample is added to a mixture of H_2O + 1,4 dioxan and a known excess of Pb^{+2} [2]. Estimation of sulphate in anodizing baths can also be done by above method using a lead sensitive electrode. Developments of SO_4^{2-}electrodes have also been reported in literature which may be useful in monitoring of SO_4^{2-}concentration in solution [39,40].

ADDITION AGENTS:

Boric Acid: A quinhydrone formaldehyde polymer coated on Pt electrode has been described

which is stable at high pH and can be used for titration of boric acid [41].

For continuous monitoring of boric acid a method based on reaction of boric acid with fluoride to produce fluoborate has been reported. A F^-ISE is used for the purpose[2].

C.T.A.B. Recently development of a silicone-base heterogeneous ISE has been reported for determation of concentration of surfactants such as CTAB in solutions [42].

Yet another report [43] which just appeared deals with the measurement of anions using surfactant Electrode. It is possible that these electrodes can contribute to the monitoring of surfactants in plating baths and therefore await evaluation.

Urea: Enzyme membranes sensitive to urea are reported in literature [44,47]. These may be useful for monitoring of urea in plating baths.

ANALYSIS OF ELECTRODEPOSITS

The electrodeposits after dissolving in a suitable medium may also be analysed for their constituents using ISEs. For analysis of brass, Chelometric titration with tetraethylene pentamine hydrochloride in ammonia background using a Cu (II) ISE has been suggested [21]

In conclusion, from above cited examples, it is clear that ISEs can be used for analyses and monitorring the constituents of baths and effluents of the metal finishing industry as well as for analysis of electrodeposits. Due to the ease of operation, precision and competitive cost they seem to be the future substitutes of conventional methods of analysis used in these industries.

ACKNOWLEDGEMENT

The authors sincerely thank Dr. V.K. Venkatesan, Scientist, and Dr H.V.K. Udupa, Director, for their keen interest in this work.

ANNEXURE

Some popular brands of ion selective electrodes useful for the metal finishing industries

Orion Research Mass. U.S.A.	Chemtrix Oregon. U.S.A.	Sensorex Calif. U S.A.	Radiometer Copenhagon	Metrimpex Hungary
1. Bromide (Solid membrane)	1. Bromide	1. Bromide	1. Bromide (Solid membrane)	1. Bromide
2. Cadmium -do-	2. Cadmium	2. Chloride	2. Chloride -do-	2. Chloride
3. Chloride -do-	3. Chloride	3. Chlorine	3. Cyanide -do-	3. Cyanide
4. Copper -do-	4. Chlorine	4 Chromium 6	4. Iodide -do-	4. Iodide
5. Cyanide -do-	5. Chromium 6	5. Copper	5. Fluoride -do-	5. Fluoride
6. Fluoride -do-	6. Copper	6. Cyanide	6. Cupric -do-	6. Silver
7. Iodide -do-	7. Cyanide	7. Hypochlorite	—	(Heterogeneous,
8. Silver -do-	8. Iodide	8. Fluoride	Universal	solid membrane)
9. Lead -do-	9. Lead	9. Iodide	Selectrode	
10. Nitrate (Liquid membrane)	10. Phosporic 5	10. Lead	1. Ag^+, Cu^{++}, Cd^{++}, Pb^{++}	
11. Fluoborate -do-	11. Silver	11. Silver	2. Cl^-, Br^-, I^-	
12. Perchlorate -do-	12. Zinc	12. Sulphate		

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