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Institut für Umwelttechnik

Institute of Environmental
Technology

**Description and Assessment of
analytical methods for
determination of chemical
substances in plating baths and
waste water for environmental
monitoring and quality
assurance**

ENCLOSURE 2

**Description and Assessment of analytical
methods for determination of chemical
substances in plating baths and
waste water for environmental
monitoring and quality
assurance**

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Muttentz October, 2004

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Acknowledgements

This thesis was funded by the Swiss Agency for Development and Cooperation (SDC), FHBB and UNIDO in the framework of the Vietnam Cleaner Production Centre support project of the Institute of Environmental Technology at FHBB.

I gratefully acknowledge my tutor: Christoph Jeiziner who reviewed the whole thesis and made many helpful suggestions.

Particularly, I honestly thank Jürg Walder who enthusiastically supported me, Antje Langbein who painstaking helped in the analytical instruction and documentation.

I also acknowledge the help and interest of a large number of FHBB/IfU employees: Maurice Jutz, Roger Giacomelli, Heinz Leuenberger for their special contributions.

Finally, I thank a lot Dr. Thomas Heim and the Institute of Environmental Technology for evaluation and support in education and training.

20th, October 2004

Nguyen Thi Thu Hien

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Preface

The environment is of special importance to the life of humans and other living creatures as well as to the economic, cultural and social development of the country, the nation and mankind as a whole.

In the recent years, environmental protection has become one of the most pressing global issues which will be put a special concentration to be solved by all the countries in the world. The environmental protection is not only the individual matter but also the main objectives for the sustainable development.

There are various causes of the environment pollution, however the main source is caused by the industrial activities which has resulted in the emission of some hazardous pollutants and has badly influenced to the ecological environment and the human health.

The research results about the current status of Vietnam environment have shown that many areas have been suffering from the environmental pollution and deterioration caused by industrial activities. Most industrial facilities in Vietnam have widely used the old technologies except some applying the advanced technologies and attracting the foreign investment.

The environmental issues has not been much paid attention and taken into a serious consideration by these industrial operations during their production activities. In Hanoi alone, there are dozens of industrial facilities where the environment problems are not satisfactorily solved, the hygienic safety standards and labour safety are seriously violated and the discharge outlets are not treated. That has caused the environmental pollution in wastewater, air and solid waste for these areas.

The main reasons for the above – mentioned current situation are:

- These industrial operations have not been fully aware of the environmental protection
- There are lack of capital investment for technological renovation
- The existing treatment systems are not suitable, whereas the technological renovation increases the pollutant treatment costs and product price which will not ensure the competitiveness in the market
- Many production facilities have not applied and complied the quality assurance and the discharge flow control

Existing and developing accompany with other industries, the electroplating industry has been playing a momentous role in the economy development in Vietnam. The increased demand of consumer items has also resulted in setting up many small-to-medium-scale plants engage in electroplating works. The growth of these independent small-scale industries in Vietnam may be attributed to the growth of light and medium engineering industries which found it more convenient and economical to have their metal products plated by independent electroplaters.

Why is metal plating so prevalent? Without metal finishing, products made from metals would last only a fraction of their present lifespan because of corrosion and wear. Finishing is also used to enhance electrical properties, to form and shape components, and to enhance the bonding of adhesives or organic coatings. Sometimes the finishes are used to meet consumer demand for a decorative appearance.

Electroplating workshop dealt in a rather broad range of end products as diverse as electronic parts (printed circuit boards, semiconductors, integrated circuits, transistors, meters, and speakers), oil drilling equipment, aircraft components, bicycle parts, typewriters, screws nuts, locks and other common household appliances.

Beside the positive effects of electroplating for the manufacture industry, it causes the main environmental pollution due to the discharge of wastewater which might be contaminated by agents such as acids, heavy metals and organic compounds. In comparison with other industries, the electroplating industry uses much less water, hence the volumes of the wastewater produced are comparatively smaller. However, the wastewater is highly toxic in nature because of the presence of metals such as copper, nickel, zinc, cadmium, chromium and cyanides. These substances easily cause substantial environmental impacts if it is not reduced and treated appropriately.

Although different ordinances and regulations regarding water discharge of waste and clean air exist in Vietnam the enforcement is still pending due to a lack of administrative personnel and tools management. One in these problems does not construct processes to take sample and measure pollution parameters. In addition adequate sampling and measurement methods for chemical substances do not exist thus, appropriate determination of contaminants is not possible.

The environmental problems of electroplating industry in Vietnam have been involving by the managers and the owner plants due to above reasons. To find correctly ways for investigating and assessing analysis and effluents control appropriately in the electroplating industry in Vietnam are most urgent matter.

The master thesis will investigate and assess appropriately analytical methods for sampling/measuring for heavy metals and effluent control technologies. These will not only limit to contaminants but also encompass components of plating baths in order to foster process control.

This thesis is organized into 5 chapters as follow:

- **Chapter 1:** Overview of the electroplating industry and environmental status of the electroplating plants in Hanoi, Vietnam
- **Chapter 2:** Analytical method for chemical substances and its analysis situation in the electroplating industry
- **Chapter 3:** Pollution prevention and effluent control technologies in the electroplating industry worldwide and in Vietnam

- **Chapter 4:** Assessment and analyzing technologies of analysis methods for heavy metals
- **Chapter 5:** Suggestion of analysis method for chemical substances and effluent control in the electroplating plants in Vietnam
- **Conclusions**

The author really desires to share experiences and cooperates with the electroplating factories and the environmental managers in Vietnam in order to find a right way as well as applying effectively these suggestions for the environmental protection of the electroplating plants.

The research will close a gap between the requirements of existing environmental law in Vietnam and the actual situation in plating industry. This work will provide an analytical package that can be used by the local industry partners and universities.

Difficulties may arise from the target group. Some methods may not be appropriate for Vietnamese plating companies as they may require too sophisticated equipment and know-how. It is, however, part of the thesis to select the most appropriate procedures and to suggest tools for their realization.

Chapter 1

Overview of electroplating industry and environmental status of the electroplating plants in Hanoi, Vietnam

I.1. Overview of electroplating industry

1.1.1. Introduction

Electroplating is often also called "electrodeposition", and the two terms are used interchangeably. As a matter of fact, "electroplating" can be considered to occur by the process of electrodeposition.

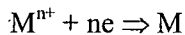
Electroplating is achieved by passing an electric current through a solution containing dissolved metal ions and the metal object to be plated. The metal object serves as the cathode in an electrochemical cell, attracting ions from the solution. Ferrous and non-ferrous metal objects are plated with a variety of metals including aluminum, brass, bronze, cadmium, copper, chromium, gold, iron, lead, nickel, platinum, silver, tin, and zinc.

The process is regulated by controlling a variety of parameters including voltage and amperage, temperature, residence times, and purity of bath solutions. Plating baths are almost always aqueous solutions, therefore, only those metals that can be reduced in aqueous solutions of their salts can be electrodeposited. The only major exception to this principle is aluminum, which can be plated from organic electrolytes.

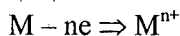
A typical electroplating cell consists of anode, cathode, aqueous-metal solution and a power supply. Nearly every metal plated is plated in the same way.

Figure 1 is a schematic presentation of an electrolytic cell for electroplating a metal "M" from an aqueous (water) solution of metal salt "MA".

Electrodeposition or electrochemical deposition (of metals or alloys) involves the reduction of metal ions from aqueous, organic, or fused salt electrolytes. In its simplest form the reaction in aqueous medium at the cathode follows the equation:



With a corresponding anodic reaction:



The anode material can either be the metal to be deposited (in this case the electrode reaction is electrodisolution that continuously supplies the metal ions) or the anode can be an inert material and the anodic reaction is oxygen evolution (in this case the plating solution is eventually depleted of metal ions).

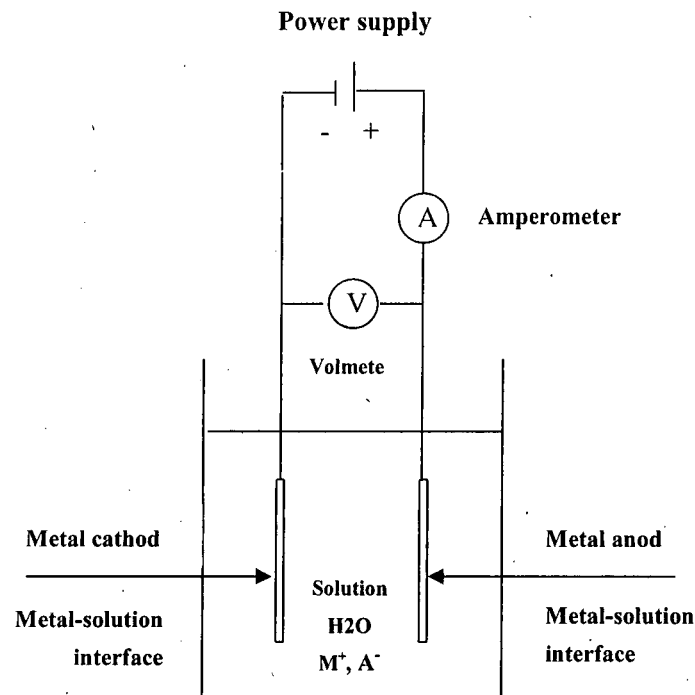


Figure 1.1. Schematic of an electrolytic cell for plating metal M from a solution of the metal salt MA

Plating operations are typically batch operations in which metal objects are dipped into a series of baths containing various reagents for achieving the required surface characteristics. Operators can either carry the workpieces on racks or in barrels. Operators mount workpieces on racks that carry the part from bath to bath. Barrels rotate in the plating solution and hold smaller parts.

1.1.2 History

The early history of electroplating may be traced back to around 1800. A university professor, or in modern terms: a chemist, Luigi Brugnatelli is considered as the first person to apply electrodeposition process to electroplate gold.

- By 1805 he had refined his process enough to plate a fine layer of gold over large silver metal objects.
- By 1839, however, scientist in Britain as well as in Russia had independently devised metal deposition processes similar to those of Brugnatelli's for copper electroplating of printing press plates.
- By 1840, this discovery was adapted and refined by Henry and George Elkington of Birmingham, England for gold and silver plating. Collaborating with their partner John Wright and using formulae developed by the latter for potassium cyanide plating baths, the Elkingtons were able to have the first viable patents for

gold and silver electroplating issued on their name. From Great Britain the electroplating process for gold and silver quickly spread throughout the rest of Europe and later to the United States.

- By the 1850's electroplating methods of bright nickel, brass, tin, and zinc were commercialized and were applied for engineering and specific commercial purposes. In time, the industrial age and financial capital had expanded from Great Britain to the rest of the world. As a result, electrodeposition processes were expanding in scope and found more and more usage in the production of a variety of goods and services. While this expansion was taking place, no significant scientific discoveries were made until the emergence of the electronic industry in the mid forties of the last century. The only exception to this was improvements made to direct current power supplies which were/are used instead of batteries.
- From 1870 to 1940 was a quiet period as far as electroplating was concerned, significant only in gradual improvement in larger scale manufacturing processes, anodic and cathodic reaction principles and plating bath formulae.

During the later years of the forties, rediscovery of heavy gold plating for electronic components took place. In comparison to that, during the mid to later fifties the usage of new and more "user friendly" plating baths based on acid formulae (rather than strongly poisonous cyanide based ones) were developed and introduced for large scale commercial use.

Today, with the impressive progress and deeper understanding of the underlying electrochemical principles of electrodeposition, sophisticated plating baths formulae have been developed and are being routinely employed.

Electrodeposition methods represent a very attractive alternative to the hitherto conventional fabrication methods.

1.1.3 Typical production processes

Electroplating operations are mostly wet processes and essentially involve pre-treatment, electroplating and post-treatment. In between these processes, rinsing is always required. A typical flow chart for general electroplating operation and attach effluents is show in Figure 1.2.

Pre - treatment

Before a workpiece is electroplated, surface contaminates such as grease and dust must be removed first. The pre- treatment stage usually involves preliminary alkaline cleaning, acid picking for removal of oxide and scale, and other surface activation methods.

Grease on the metal workpiece usually comes from machining, stamping, polishing and preservation stages. Grease of organic nature is removed by saponification with alkali. Petroleum and mineral oil grease cannot be removed by this method and trichloroethylene, benzene, gasoline and carbon tetrachloride are employed. But the most commonly employed method of degreasing is emulsification with alkalis. These are

usually mixtures of sodium carbonate, caustic soda, trisodium phosphate, sodium silicate, sodium cyanide and borax.

Removal of rust and scale from iron articles is usually carried out by pickling with sulphuric acid or hydrochloric acid. Lately, the electrolytic method of striping has been increasingly used because of its rapid action. In this method, the material to be plated is made the anode. The end-products in both the processes are essentially the same. Fine sand particles remaining on the surface due to sand blasting can be removed separately by hydrofluoric acid.

Electroplating

The electroplating process is the deposition of a thin metal coating on an electrically conductive surface, for decorative or corrosion prevention purposes.

Plating baths are acidic in nature and generally contain sulphuric, hydrochloric or nitric acids. Alkaline baths containing sulphide, carbonate, cyanide and hydroxide are also used.

Post - treatment

The main operation carried out in the post treatment stage are drying of the workpieces and final inspection. In some cases, the plated products may be required to undergo a series of post treatments such as conversion coating or paint spraying to provide a protective coat.

Rinsing

Rinsing always employed after each processes:

- After the cleaner work is rinsed to avoid neutralization of the pick.
- After the pick, workpiece is rinsed to avoid contamination of the plating tank. and,
- After plating the workpiece is rinsed to avoid spotting and staining

They are first dipped in stationary water baths, allowed to drain and then dipped in running water baths to remove the adhering plating solution known as "drag-out".

The quality of drag-out depends upon the nature of the solution, its temperature, shape of the material being plated and the time allowed for draining. Manual plants are known to have higher drag-out losses than automatic ones.

Rinsing usually takes place in large series of process tanks in a plating line. Each process solution from the parts is usually followed by a set of rinse tanks for the removal of residual process solution from the parts and the prevention of contamination across different baths.

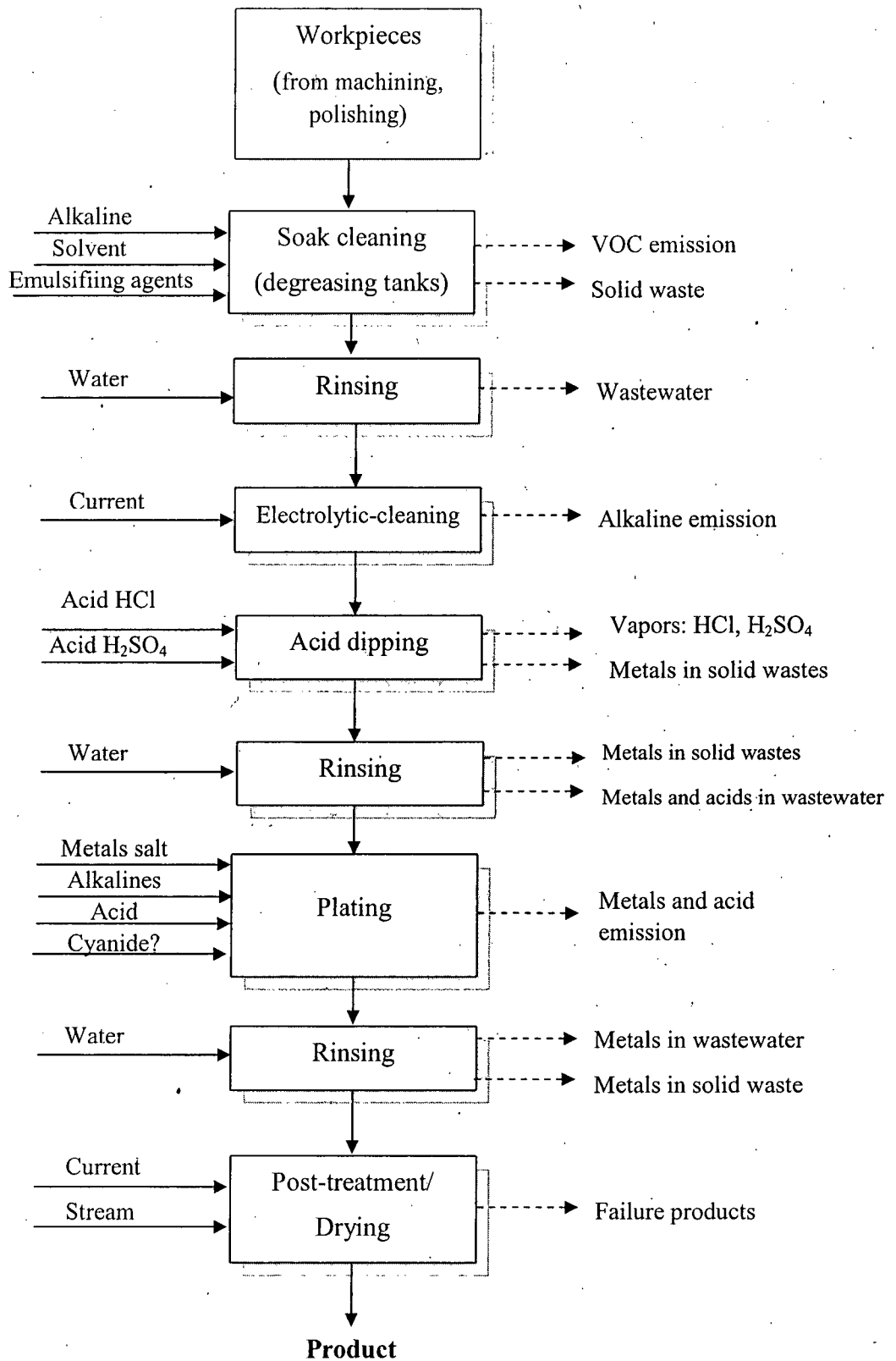


Figure 1.2 A Typical Process Flow Diagram for Electroplating Operation

1.1.4 Manufacture problems

Plating problems caused by pitting, poor adhesion, brittle deposits, and rough deposits can result in rejects. Rejects due to defects in plating can be costly, since rejected parts must be either replaced or stripped and re-plated; effectively, generating two or more times the waste beyond normal operation. While there are many factors contributing to poor performance, Table 1.1 lists the more typical ones. Inorganic contaminants can affect the metal plating solution causing undesirable appearances (dark deposits in low current density areas), poor adhesion and roughness.

Table 1. 1. Plating problems and potential cause

Problem	Potential cause
Pitting	pH too low, inadequate agitation, current density too high, low wetting agent content, organic contamination, copper contamination, poor surface preparation.
Poor adhesion	Poor cleaning/rinsing, hexavalent chromium, contaminated picking acid
Brittle deposits	pH too high, organic contamination, high sodium content, high chloride content.
Rough deposits	Calcium contamination, torn anod bag, poor filtration

Purification processes, such as carbon treatment and low current density dummyming (plating at very low current density onto scrap steel sheets) are used to remove common metallic and inorganic contaminants, such as copper and zinc.

Water that is used in plating process also plays an important role to improve plating quality. All inorganic and organic contaminations in water influence the plating tanks and quality product directly.

Table 1. 2. Affect of impurities in water onto plating tanks [13]

Plating solution	Ca	Mg	Na	Fe	Carbonate salt	Organics
Chromium		4	4	4		6
Acid copper				2		
Cyanide copper	1	1		1		8
Nickel sulphate	1		9	2;7;8	8	3;7
Cyanide zinc	1,2	1				
Sulphate zinc				9		

- | | |
|---|----------------------------|
| 1: Deposited | 6: Reduce Cr ⁶⁺ |
| 2: Rough layer | 7: Spot |
| 3: Dull layer. | 8: Blister |
| 4: Reduce distribution ability of layer | 9: effect of process lower |
| 5: layer can be fail | |

Contaminants in water are usually low; however by time water will evaporate therefore in the baths still have impurities. Gradually, impurities are accumulated more concentrated which affect the product quality.

1.1.5 Sources and characteristics of electroplating waste

Wastewater

The electroplating processes usually generate a considerable amount of liquid waste everyday. The two major sources of wastewater in the electroplating operations come from batch solutions and rinse water. They are distinctly deferent in volume and characteristics.

Electroplating effluents include toxic compounds like cyanide and heavy metals, and vary greatly in pH. Chemical wastes like spent alkaline degreasing solutions, spent pickling acids, spent solvents, etc. are also common undesirable by-products. Table 1.3 summarizes the typical pollutants and pollution sources of typical electroplating operation.

Table 1.3 Pollutants in wastewater and pollution sources in electroplating operation

Common pollutants	Major pollution Sources	Potential hazards
Alkalis: NaOH, KOH, Na ₂ CO ₃ , silicates, alkaline phosphates	Dewaxing, soak cleaning, electrocleaning, neutralization	Corrosivity
Acids: H ₂ SO ₄ , HCl, HNO ₃ , HF, H ₃ PO ₄ , acid acetic	Acid dip, picking, etching	Corrosivity
Organics: Oil, grease, organic solvents (perchloroethylene, trichloroethylene...), complexing agents	Dewaxing, soak cleaning, electrocleaning, plating baths containing chelating, brightening and wetting agents	Aquatic Toxicity
Suspended solids: Sand, dust, silicates	Cleaning, pickling, rinsing water	
Cyanide wastes: NaCN, KCN, Cu(CN) ₂ , Zn(CN) ₂ , AgCN, AuKCN, Cd(CN) ₂	Cleaning, copper plating, zinc plating, silver plating, gold plating, cadmium plating	Toxicity
Heavy metal containing waste: Cu, Ni, Fe, Zn, Pb, Ag, Mn, Cr, Zn, boron, etc.	Spent plating baths, rinsing water	Toxicity
Chromium waste	Chromium plating, etching, passivation	Toxicity

The volume and characteristics of various wastewater stream vary considerably from one plating plant to another and within the same plant from day to day. Generally, the drains inside the plants are interconnected mainly due to facility layout of the plant and partly to ignorance of the consequences. Table 1.4 summarizes the volumes and characteristics of wastewater from electroplating workshop. The ranges of concentration of pollutants in wastewater are:

Cyanide:	1.0 to 150 mg/l
Chromium:	0.25 to 2.6 mg/l
Copper:	0.74 to 75 mg/l
Nickel:	0.07 to 125 mg/l
Zinc:	0.12 to 140 mg/l
Lead:	1.45 to 20 mg/l
Tin:	10.0 to 20 mg/l
Iron:	0.17 to 300 mg/l

The electroplating wastes may be acidic or alkaline depending on the type of baths used. Result from Table 1.4 indicates that they may be highly acidic with a pH of 1 or highly alkaline with pH of 12. Total dissolved solids and total suspended solids range from 131 mg/l to 19.500 mg/l and 1 mg/l to 3.160 mg/l, respectively.

Table 1.4 Characteristics of wastewaters discharged from electroplating processes for electroplating industry [2]

Plating shop	Waste flow (m ³ /day)	pH	Total dissolved solids	Total suspended solids	COD	Cyanides	Total of metals content	Cu	Ni	Cd	Zn	Pb	Sn	Cr ⁶⁺	Ag	Fe	SO ₄ ³⁻	Cl ⁻	PO ₄ ³⁻
1	18.7	3.5	1560	283	308	83	-	-	-	-	23.6	35.5	-	1862	-	-	-	-	-
2	11.8	2.5	17500	560	-	40	-	75	100	-	-	-	20	-	-	-	-	-	-
3	5.6	2.8	715	40	55	70	-	-	-	-	-	-	-	52.5	-	-	-	-	-
4	22.4	2.0	1271	29	-	-	-	-	6.2	-	110	-	-	27.5	-	-	-	-	-
5	22.4	2.0	6617	29	-	-	-	-	0.64	-	-	-	-	652	-	-	2880	2450	-
6	20	1.9	921	6	83	2.2	-	0.85	32	-	24	-	-	2600	-	-	-	-	-
7	5	2.7	352	1.4	81	1.27	-	-	0.07	-	7.0	-	-	1990	-	-	-	-	-
8	10	12.0	1392	3	97	1.79	-	-	0.12	-	0.12	-	-	1730	-	-	-	-	-
9	254	4.0	-	400	-	150	50	-	-	-	5.0	-	-	25	-	-	-	-	-
10	91	2.0	-	-	-	-	-	10	-	-	-	-	-	-	-	-	-	-	-
11	37	6.0	4606	3160	151	-	-	-	-	-	140	-	-	-	-	-	-	-	132
12	270	9.0	2400	300	500	30	-	40	50	-	-	50	-	-	-	-	-	-	-
13	40.8	4.0	2000	56	126	5.0	-	-	-	-	18	-	-	-	-	-	-	-	-
14	950	9.0	2580	650	383	50	-	50	20	-	60	25	15	-	10	300	-	-	-
15	450	8.0	2800	350	520	5.0	20	-	-	-	-	-	-	-	-	-	-	-	-
16	42	1.0	-	-	-	1.0	-	1.0	-	1.0	-	-	-	50	-	-	-	-	-
17	60	2.0	2580	279	138	-	-	58.3	-	-	-	-	-	-	-	-	-	-	-
18	55	3.0	836	136	203	-	-	-	-	-	-	-	-	0.25	-	-	-	-	-
19	15	4.0	1500	380	40	150	-	60	30	-	50	-	-	-	-	-	-	-	-
20	90	9.7	4930	51	643	-	-	26	125	-	-	1.45	17.5	-	-	-	3075	835	-
21	130	10.7	816	150	868	73	-	-	0.20	-	-	-	-	-	-	0.63	-	-	-
22	25	2.8	560	4.2	12	-	-	-	-	-	-	-	-	100	-	-	-	-	-
23	55	3.0	1377	10	392	-	-	-	0.85	-	-	-	-	5.13	-	-	-	-	-
24	350	3.0	350	267	50	-	5.0	-	-	-	-	-	-	-	-	-	-	-	-
25	540	3.0	2885	360	550	-	-	-	-	-	-	-	10	-	-	-	-	-	-
26	41	5.8	131	1.2	-	-	-	0.74	-	-	-	-	-	-	-	0.17	-	-	-
27	1400	2.0	1000	1000	81	-	-	50	-	-	-	-	-	-	-	-	-	-	-
28	800	3.8	3125	989	321	-	-	-	17.6	-	-	-	-	-	-	-	-	-	-

All results except pH are expressed in mg/l.

Air Emissions

Air emissions from plating operations are generated in the form of mists during the process due to the evolution of hydrogen and oxygen gas and acidic fumes from highly acidic processes. Hydrogen gas bubbles are formed in the process tanks on the surface of the submerged part or on anodes and/or cathodes. These gas bubbles rise through the plating solution and “burst” upon reaching the surface escaping into the air forming a mist.

There are a number of factors that determine the rate of gassing, including the temperature of the solution, the current densities in the plating tank, the solution composition, solution pH, the surface area of the parts being processed, and the surface tension of the plating solution. Air sparging can also result in emissions from the bursting of air bubbles at the surface of the plating tank liquid. Usually, plating baths (other than strikes) have high cathode efficiencies, so the generation of mist in plating is minimal.

Other air emissions, such as volatile organic compounds (VOCs), may be generated in preparing the parts for plating from degreasing, solvent cleaning, and open containers of solvents. There also may be emissions from exhaust ventilation, spills or leaks, and, especially, from stripping of rejects. The most commonly used stripping solutions are either nitric acid or sulphuric acid.

Cyanide-based stripping solutions may also be used. These solutions have a high temperature and are without current. Air emissions from cyanide-based stripping solutions may include ammonia from decomposition of cyanide.

Toxic and Hazardous Wastes

Most toxic and hazardous wastes are generated during the cleaning part of the process. More specifically, surfactants are used to remove oil and grease, plating solutions are contaminated beyond beneficial reuse, and sludge that contains metals is formed as a result of wastewater treatment. Absorbents, filters, filter cakes; still bottoms, contaminated solvent, carbon, wipe rags, aisle grates, and abrasives are generated solid wastes that are potentially hazardous.

Wastes that exhibit toxic characteristics defined by the presence of metal ions and other organic compounds, which are eventually placed in a landfill, would likely leach hazardous concentrations of these toxic constituents into the environment. Wastes must be handled and discarded in a hazardous waste landfill to restrict leaching into groundwater or surrounding soils.

1.1.6 Environmental impacts

Metals and chemicals are two major materials used in the electroplating industry. The release or dumping of chemical residues and effluent can create a wide range of environmental damages and causing serious human health effects. These effects may vary from the target species to another, and also depend on the pathway that a chemical takes in the environment. Many chemicals such as heavy metal may accumulate in the human body and show detrimental effects years after exposure has begun.

The discharge of untreated electroplating wastewater to natural waterways has contributed to water pollution in many industrial regions. As well as damaging natural ecosystem, the water has often become unfit for drinking. Fisheries may be directly destroyed, or their products rendered unfit for eating.

Some chemical toxicants in electroplating wastewater such as alkaline, CN⁻ and other metals which effect directly on fish and fish food given in Table 1.5.

Table 1.5 Toxicity of plating wastewater constituents to fish and fish food [3]

<i>Substance</i>	<i>Concentration (mg/l)</i>	<i>Test organism</i>	<i>Effect</i>
Nickel chloride	4.5 (as Ni)	Gold fish	Kills in 200 hrs
Lead nitrate	63 (as Pb)	Gold fish	Kills in 80 hrs
Stannous chloride	626 (as Sn)	Gold fish	Kills in 45 hrs
Zinc sulphate	25 (as Zn)	Trout	Kills in 133 minute
Zinc (ion)	0.3 (as Zn)	Fish	Kills some fresh
Sodium cyanide	0.3 (as CN)	Minnows, flatfish carp	No affect in 24 hrs
Potassium cyanide	0.04-0.12 (as CN)	Goldfish	Kills in 3-4 days
Cyanogens chloride	0.08 (as CNCl)	Fish	Critical
Potassium ferrocyanide	948 (as CN)	Minnows, goldfish	Not lethal
Ammonia	2.5 (as NH ₃)	Goldfish	Kills 1-4 days
Ammonia	2.7 (as NH ₃)	Fish	Lethal
Hydrogen sulphide	10 (as H ₂ S)	Goldfish	Kills in 96 hrs
Sulphide (ion)	3 (as S)	Trout, fingerings	Kills in 5 minutes
Sulfide (ion)	0.5 – 1.0 (as S)	Fish	Critical
Potassium cyanide	265 (as KCNO)	Trout, fingerings, adult minnows	No effects in 24 hrs
Sodium hydroxide	156 (as NaOH)	Daphnia magma	Toxic
Trisodium phosphat	52 (as Na ₃ PO ₄)	Daphnia magma	Toxic
Chlorine	0.05-1.0 (as Cl)	Fish	Critical

- *Daphnia magma is a representative fish food organism commonly*

Complexing agents are primarily used as additives in electroplating or metallizing baths, in picking, degreasing and cleansing dips, in etching and demetallizing solutions and photographic baths. As a consequence, the chelated heavy metal ions are kept in solution in the effluent as well. If the complexing agent is not destroyed or masked with regard to its normal effect during effluent treatment, the metals can pass only by slow biological metabolism potentially releasing corresponding metal ion, highly toxic to both fish and microorganisms (see table 1.6). In some cases, they even exceed the toxicity of compounds like cyanides.

Table 1.6 Toxicity factors of various toxins in electroplating effluents, referred to KCN = 1

Toxin	Calculated as	Fish	Daphnia	Escherichia coli
KCN	CN ⁻	1.0	1.0	1.0
KOCN	CN ⁻	0.0013	0.14	1.6
K ₃ Cu(CN) ₄	CN ⁻	0.1	6.25	0.2
K ₂ Ni(CN) ₄	CN ⁻	0.003	0.37	0.8
K ₂ Zn(CN) ₄	CN ⁻	0.3	0.7	< 0.1
K ₂ Cd(CN) ₄	CN ⁻	0.15	10.0	2.0
CuSO ₄	Cu ²⁺	0.7	125.0	2.0
NiSO ₄	Ni ²⁺	0.002	0.91	2.5
ZnSO ₄	Zn ²⁺	0.007	0.42	2.5
CdSO ₄	Cd ²⁺	0.004	10.0	1.0
KCr(SO ₄) ₂	Cr ³⁺	0.001	0.125	5.0
K ₂ CrO ₄	Cr ⁶⁺	0.0003	2.0	2.0

• Source: R. Weiner, "Galvanotechnik" 67 (1976) N^o 8, pgs. 646-648

Purification of water to restore its use is generally expensive. To reduce problems local pollution, many cities provide a public sewage system for wastewaters. However, if such wastewater are too concentrated, the discharge into public drains and sewers can still cause problems. Toxic chemicals can interfere with the purification process of treatment systems. Heavy metals contained in effluents often accumulate in the sewage sludge. If used as soil conditioners on farms, the heavy metal bearing sludge can pass the chemicals on to plants or to animal feed.

1.1.7. Environmental management system and quality assurance

Environmental management system (EMS) and quality management (QMS) have been designed as a practical tool to assist plating companies to identify, assess and subsequently manage their environmental responsibility and quality management. Faced with stricter environmental legislation and pressure from customers to improve their environmental performance, metal finisher are becoming increasingly aware of the cost savings and other benefits with result from establishing continuous improvement programmes.

Many metal finisher have previously relied on an approach to environmental issues. They have tended to consider and address issues such as health and safety, emission limits and noise pollution in isolation. However, there are many advantages to be gained through the adoption of a more integrated approach to managing all these concerns.

Setting up an environmental management system (EMS) will provide a company with a frame work through which its environmental performance can be controlled and improved.

ISO 9000 and ISO 14000 families are among ISO most widely known standards ever. ISO 9000 and ISO 14000 standards are implemented by some 634000 organizations in 152 countries. ISO 9000 family is primarily concerned with "quality management" and ISO 14000 families is primarily concerned with "environmental management".

An EMS contains several features present quality management system (QMS). Both systems concerns closely and they are both concerned fundamentally with ensuring that specific management objective are met.

Benefits that companies can get are: improved environmental performance, enhance compliance, prevention of pollution, new customer, increase efficiency, reduced costs, employee awareness of environmental issues and responsibilities etc.

Assessing how well the system is performing so have to monitoring and measurement. EMS and QMS cannot implement without effective monitoring and measurement processes. Monitoring and measurement enables an organization to:

- Evaluate environmental performance
- Analyse root causes of problems
- Assess compliance with legal requirements
- Identify areas requiring corrective action, and
- Improve performance and increase efficiency

In short, monitoring helps companies manage their organization better. Pollution prevention and other strategic opportunities are identified more readily when current and reliable data is available.

Recently, some plating companies in Vietnam have been gradually applying EMS and QMS. However, ISO 9000 is commonly using in order to their products can comparative in market.

About implementing ISO 14000 have just registered by few companies due to the owners of companies recognizes that they have to invest high initial cost and this take them a long time to employ. Therefore, implementing monitoring and measuring for pollution parameters in these companies are infrequent. In future, the companies should realize this matter, if companies have a good implement, not only reduce environmental pollution but also improve quality products. These bring many benefits for companies themselves.

I.2 environmental status of electroplating plants in Hanoi, vietnam

I.2.1 General Situation

Electroplating factories in Vietnam are mostly small and medium-sized enterprises, branches that concentrated commonly in the big cities such as HaNoi, Hai Phong, Ho Chi Minh... Most of electroplating plants in Vietnam have no inadequate treatment facilities. The main factors are their sporadic distribution of small-scale operation, lack of space for installing waste treatment facility and the high capital and recurring costs of treatment to meet the effluent guidelines particularly for the small workshop.

Hanoi is Vietnam' capital in which centers of the economical, political culture almost concentrated there. Therefore, in order to compare with the environmental problems of the electroplating plans in the whole country, basically, the electroplating industry status in Hanoi is typical and the same than in other cities.

At the present time, Hanoi has more 300 industry factories of which 200 are located within the urban area, 15700 plants produce are small scale industry, that they almost in backward situation, have been down graded. The old industries are also dispersed, and due to expanding urbanization and growth of urban centers most of these industries are located within urban areas of many towns and cities. Recently, electroplating industry in Hanoi there are some plants which have been step by step investing and innovating technology, improving environment and raising quantity products. Generally, electroplating industry in Hanoi is still old technology and do not meet the standards of environmental quality. Most industry plants in the city in which wastes treated not appropriately, in addition to weakness infrastructures and overpopulated who are living in the city. These have been causing pollution problems seriously and becoming the most interested of the administration in the city.

A typical characteristic of electroplating companies in Hanoi is almost production-lines installed in 1970s (Minh Khai lock company, VietTiep lock company...). Using old technology lead to the active power of the system is not great enough and consumes a lot of chemicals. Apart from arrangements of layout not only is not sensible but also effect on the splitting of effluents. Furthermore, many companies have not been arranged in the same area, this causes a big difficult for concentrating wastes to treat.

Based on the statistic data of Hanoi Department for Science Technology and Environment, the main characteristic of some electroplating factories in Hanoi may be summarized (table 1.7)

Table 1.7. Statistics of the main characteristics of some electroplating companies in Hanoi

No	Name	Products		The main waste cause air pollution	The main waste cause water pollution
		Kind of products	Quantity products/year		
1	Minh Khai lock company	quays, locks, hinges	1.500.000	Dust, Cr vapour, CO, CO ₂ , NO ₂	NaOH, PO ₄ ³⁻ , Na ₂ SO ₃ , H ₃ PO ₄ , H ₂ SO ₄ , HNO ₃ , CrO ₃ , oil
2	1 Instrument Company, Nguyen Trai street, Thanh Xuan, District-Hanoi	Srew-cuttler, iron equipment	165 tons	Dust, HCl, Na ₂ SO ₄ , H ₂ SO ₄	Oil, impurities
3	Thermost flast Rang Dong, Ha Noi	Light bulb, themost flast	11.000	Dust, SO ₂ , CO, CO ₂ , NO ₂	Acid, mercury, oil
4	Metal Thang Long Company	Oil stove, cover for street light, traffic lights, marker lamp	2.700.000	Dust, SO ₂ , CO, CO ₂	Cr, Ni and others
5	Viet Tiep lock company, Hai Ba Trung District, Hanoi, Vietnam	Kind of locks	3.000.000	dust, acid stream, alkali stream and metal vapour	acid, alkali, Cu(CN) ₂ , PO ₄ ³⁻ , CN, Cr, and other salt metals
6	Goshi - Thang Long accessories company	Accessories for motobike, car	3.000.000	Dust, SO ₂ , NO ₂ , CO, solvent vapour	Cr, Ni, oil and grease and other metals
7	Repair motorbike, car Ha Noi	Accessories for motobike, car	100 tons	Dust, SO ₂ , NO ₂ , CO, solvent vapour	Cr, Ni, oil and grease and impurities
8	Dong Da Motorcycle-bicycle Company	Accessories for motobike, bicycle	2.300.000	Dust, CO, SO ₂ , HCl	oil, Cr, Ni, CN, Cl ₂
9	Sigh and equipment for urban Company	Mechanic equipment	1.200.000	Dust, acid vapour	Oil, grease and some heavy metals
10	Thong Nhat Electro mechanics Company	Electric - fans	3.400.000	solvent, pain, alkali vapour, acid vapour	Oil, grease and Cr, Ni

1.2.2 General Characteristics of waste sources

At the same time, products of electroplating industry in Hanoi include nickel plating, copper plating, zinc plating, chromium plating and silver plating. In addition to several workshops have been plating alloys. However, in fact, the products of the companies and the individual plants in Hanoi are mainly being plated by Cu, Cr, Ni, and Zn.

Characteristics of gas wastes

Gas wastes have mainly constituents and the sources as follow:

- Chromic mist from Cr baths
- Cyanide mist from Cu bath, Zn bath with cyanide.
- Acid vapor: from stripping bath, polishing electrochemistry, etching, Cr bath...main vapors are H_2SO_4 , H_3PO_4 , HCl, HNO_3 .
- Alkali vapor: De-greasing bath.
- Solvents vapor: stemming from cleaning processes. Mainly: trichoethylen, pechloethylene, petroleum.
- Gas from burning coal oven

According to investment results, waste gases constituents of some plants that have been using the electroplating processes and finishing processes in Hanoi area are given in table 1.8.

Table 1.8. The constituent of waste gases of some companies electroplating in Hanoi [6]

No	Name of company	Inside of workshop (mg/m ³)							Outside (mg/m ³)							Collect ed years
		Dust	NO _x	SO ₂	CrO ₃	NiO	CO	Dust	NO _x	SO ₂	CrO ₃	NiO	CO			
1	Minh Khai lock company	6.1	0.01	0.03	0.00	0.00	0.1	0.57	0.005	0.02	0.003	0.003	12	2001		
2	Viet Tiep lock company	1.77	-	0.04	0.02	0.01	-	0.52	-	0.020	0.005	-	-	1997		
3	Thang Long Goshi accessories company	0.47	0.02	0.02	-	-	3.4	0.26	trace	0.009	-	-	1.4	1997		
4	Thermost flast Rang Dong, Ha Noi	-	-	-	-	-	-	0.50	0.029	0.112	-	-	3.24	1998		
5	Metal Thang Long Company	0.9	0.1	1.36	0.01	-	2.3	0.8	0.020	0.075	-	-	1.55	1998		
6	Equipment for measuring and cutting Company	0.8	-	0.8	-	-	10	0.2	-	0.4	-	-	5	1996		
7	Metal Cau Buou Company	0.53	-	0.02	0.00	-	-	0.2	-	0.156	0.000	-	-	1996		
8	Thong Nhar Electromechanics Company	0.97	0.5	0.7	0.05	-	0.4	-	0.6	0.004	-	-	-	1996		
9	Repair motor car Ha Noi	6.8	-	3.5	0.23	0.01	-	0.78	-	4.3	0.032	-	-	1996		
10	Dong Da Motorcycle-bicycle Company	-	-	2.1	0.1	-	0.0	-	0.1	0.4	-	-	-	1997		
11	Giai Phong mechanic Company	0.32	-	0.67	0.2	-	1.4	0.25	0.12	0.016	-	-	4	1998		
	Standard Vietnam (5937,	6	5	2	0.1	0.5	30	0.3	0.1	0.3	0.001	-	5			

FHBB

5938-1995,
column B)

5

Notes:

Standard Vietnam 5937-1995: Air quality - Ambient air quality standards

Standard Vietnam 5938-1995: Air quality - Industrial emission standards - Inorganic substances and dusts

Generally, waste sources of electroplating companies in Hanoi have rather high concentration such as: SO_2 , CrO_3 , NiO . Furthermore concentration acids steam, dust in the ambient area of plants is higher than environmental standard (Minh Khai company = 0,57, repair motorcar Hanoi = 0,78). All these will cause the environmental pollution inside area of workshop and the environmental ambient in Hanoi.

Characteristics of wastewater from industrial electroplating in Hanoi

Wastewater stemming from electroplating plants has multiple constituents, concentration of toxicants always changes in a large range, pH also vary from acid to neuter or alkaline. However, wastewater from electroplating plants is splited into 3 classifies:

- Alkaline or acid wastewater
- Wastewater from baths without cyanide
- Wastewater from baths with cyanide

Practically, the investment to assess environmental status of plating plants have met more difficult because the owners of plants have no self-aware to implement environment law and regulations. This has lack of data about constituents, concentration of chemical toxicants in wastewater of some plants.

Following is data for constituent of parameters in wastewater of some of the electroplating companies in Hanoi (given in Table 1.9)

Table 1.9 Characteristics of wastewater constituent in some companies in Hanoi [6]

No	Name	Tem. (°C)	pH	flow m ³ /month	Ni ²⁺ (mg/l)	Cr (mg/l)	Cu (mg/l)	CN ⁻ (mg/l)	COD (mg/l)	Zn ²⁺ (mg/l)	Fe (mg/l)	Collected years
1	Thang Long Goshi accessories company*	25-26	5-7.5	100	0.02-0.23	100-500	0.13-0.17	< 0.1	320-384	-	-	1999
2	Minh Khai lock company *	21-23	6.3-7.5	70	1.2	0.08	0.2-0.6	-	42	2.5	1,47	2003
3	Viet Tiep lock company *	20-22	6.8	70-80	0.9-1.5	2.5-3.4	-	0.16	125-135	-	0.5-0.8	2001
4	Thong Nhat Electromechanics company	24	5.8	55-60	0.62	0.109	0.037	-	28.5	-	-	1999
5	Metal Thang Long Company*	24	10.8	40	16.00	8.8	0.55	0.039	112	-	-	1999
6	Thong Nhat Motorcycle- bicycle Company *	25	6-6.5	-	1.45-2.14	9.3-12.4	-	0.03	-	-	-	2001
7	Bicycle Xuan Hoa Company*	-	-	-	2.5	0.12	-	-	-	-	0,12	2003
8	Giai Phong machinery company	24	7.7	50	-	-	-	-	32.5	-	-	1997
Standard Vietnam 1945 -1995 (Column B)		40	5.5-9	-	1	0.1	1	0.1	100	-	-	

Note:

*: Company had wastewater treatment

Wastewater in electroplating industry contains toxicological pollutants Cr, Ni, Cu, CN, Zn. This is very danger because these substances are highly toxic and can accumulate in sediment.

Figures that given are scattered, not continues, unreliability and not note analytical methods. However, most companies have wastewater treatment systems but the outlet quality is still higher than the discharge standards. Implementation monitoring of pollution parameters is rarely, only once or twice during operation time of system. Hence, it is really to understand that if have any body ask whether changing for constituent parameters in wastewater or not so both management offices and companies do not known.

Characteristic of solid waste of electroplating in Hanoi area

Electroplating in Hanoi area have a lot kind of products as: plate for restoring old workpieces, plate material for construction, lock etc, so they have many kind of solid wastes. The mainly solid waste: coating paint cover, scale, rust, solid waste from waste treatment system contain heavy metals.

The most important of solid waste is sludge from waste water treatment because it contains more heavy metal than all.

Table 1.10 Load waste sludge and concentration heavy metals in its of some companies electroplating [10]

No	Name plants	Amount sludge (ton/year)	Load of heavy metals (kg/year)				
			Fe	Ni	Cr	Cu	Zn
1	Minh Khai lock company	60 - 75	7.2 - 9	51 - 64.5	6.10^{-5} - $7.5.10^{-5}$	-	-
2	Thang Long metal company	130 - 276	60.2	17.9-90.09	42.13-116.3	1.05	0.643
3	Ghoshi Thang Long company	70 - 90	2.82 - 3.65	2.52-3.24	0.344-0.442	-	-
4	Viet Tiep lock company	300	-	2.20 - 253	0.462 - 0.53	3.255-3.72	-

According to the statistic data of Hanoi Company for Environmental Urban estimated approximatively amount waste sludge for 7 companies have Cr, Ni workshops with supposing all companies have got waste water treatment system:

Table 1.11. Estimation of Loading sludge of 7 companies in Hanoi, approximately

No	Kind of sludge	Load (ton/year)
1	Total of sludge contain Cr ³⁺	19,525 – 32,544
2	Total of sludge contain Ni	6,262 – 7,008
3	Total of sludge contain Zn and Cr ³⁺	105,822
	Total sludge for plating processes	132 – 145

See table 10, we can realize that, the amount of waste sludge is not high. For electroplating workshops a wastewater treatment system by chemical methods is essentially, waste sludge is highly toxic. This sludge is more difficult for biological decay because heavy metals are toxic for microorganisms.

Generally, tank residues from the metal plating processes have to be transported off-site for treatment and disposal because they are typically defined as characteristic hazardous wastes.

I.2.3 Affects of the wastewater of electroplating industry in Hanoi to environment

Until now, most industrial wastewater in Hanoi (even wastewater of the electroplating industry) is directly released into domestic wastewater drainage of Hanoi city. These are remarkable contribution for causing contaminant groundwater and surface water of Hanoi. The waste water of electroplating industry also is cause to increase heavy metals constituents in water system of the city. Results were invested in sediments of rivers system drainage of Hanoi given in Table 1.12

Table 1.12 Content (ppm) heavy metals in sediment water in river system drainage in Hanoi [6]

No	Cu		Pb		Cr		Ni		As		Cd		Hg	
	Soluble	Sediment	Soluble	Sediment	Soluble	Sediment	Soluble	Sediment	Soluble	Sediment	Soluble	Sediment	Soluble	Sediment
1	0.068	0.013	0.021	0.009	0.028	0.034	0.026	0.050	0.013	0.001	0.001	0.002	0.001	0.001
2	0.030	0.031	0.013	0.033	0.030	0.032	0.042	0.062	0.016	0.001	0.001	0.001	0.001	0.001
3	0.013	0.013	0.007	0.009	0.022	0.024	0.037	0.059	0.018	0.001	0.001	0.002	0.001	0.001
4	0.039	0.040	0.039	0.036	0.031	0.064	0.026	0.047	0.026	0.001	0.001	0.003	0.001	0.001
5	0.072	0.062	0.029	0.065	0.032	0.053	0.045	0.058	0.021	0.001	0.001	0.002	0.001	0.001
6	0.016	0.059	0.011	0.065	0.023	0.058	0.029	0.066	0.019	0.001	0.001	0.004	0.001	0.001
7	0.025	0.036	0.010	0.051	0.026	0.033	0.039	0.073	0.019	0.001	0.001	0.002	0.001	0.001
8	0.021	0.040	0.012	0.019	0.025	0.026	0.033	0.039	0.043	0.019	0.001	0.001	0.001	0.001
9	0.013	0.029	0.006	0.040	0.029	0.028	0.023	0.061	0.013	0.001	0.001	0.002	0.001	0.001
10	0.012	0.019	0.008	0.041	0.032	0.021	0.025	0.063	0.040	0.001	0.001	0.002	0.001	0.001
11	0.021	0.023	0.014	0.039	0.027	0.027	0.026	0.045	0.017	0.001	0.001	0.004	0.001	0.001
12	0.012	0.025	0.007	0.030	0.024	0.040	0.028	0.046	0.010	0.001	0.001	0.002	0.001	0.001
13	0.022	0.068	0.007	0.060	0.029	0.035	0.034	0.050	0.031	0.001	0.001	0.003	0.001	0.001
14	0.015	0.033	0.016	0.042	0.029	0.028	0.020	0.036	0.020	0.001	0.001	0.002	0.001	0.001

Notes:

1: Khuong Dinh Bridge	8 Set
2: Dau Bridge	9 So Thuong Bridge
3: Thanh Liet Bridge	10 Tu Hiep
4: Mai Dong Bridge	11 Van Dien Bridge
5: Vinh Tuy-Kim Nguu ditch	12 Bang Ba
6: Yen So	13 Quynh Do Bridge
7: Set Bridge	14 Tho An Bridge

The results above shows that rivers in Hanoi areas are contaminated seriously, the content of heavy metals in the sludge is rather high due to the water of river is in the weak- base area, so the heavy metals exist mainly as hydroxide and salt base settled into bottom of the rivers.

Although have a lot information about pollution level of heavy metals and organics in rivers, drainage water system of city but these data were too old, scattered. So to assess affects of wastes in the electroplating industry into environment is not enough clearly which can have many difficulties for managers when adopting environmental policies. Based on data, managers can specific definite the pollution level of each company and electroplating referred to environment.

I.2.4. The Impact of the electroplating industry wastewater to discharge standard and environment

Environmental Law Vietnam was adopted on 27 December 1993 by National Assembly and applied on 1 October 1994. It includes 55 articles and followed by decrees, that provides for the protection of the environment in Viet Nam. At the present time, Vietnam government have been applying decree no 67/2003/ND-CP on environmental protection charges for wastewater. Environmental Standard also began to implement in 1995 as well. All wastes that discharged into environment have to treat correctly that to approach standard levels.

However, discharge wastewater standard for all of industries are being applied together and they also use the same discharge limit concentration of the parameters. This is really difficult for the owner enterprise and most organizations have been working on the field of the environmental protection.

The obvious Discharge standard for the wastewater in electroplating in developed countries such as Germany, Switzerland, USA, Brittan, Australian and several countries in Asian as Thailand, Singapore, etc are given in annex.

The standard discharge all above countries were built base on kind of processes, the industrial scale production, ensured their legitimate right and depending on foundation progressive industry.

Hence Vietnam conditions have no facilities produce, backward technology and the production processes have no both mechanize and automatics, therefore most of plants in Vietnam have not complied all processes about protection and prevention pollution.

Furthermore, the wastewater from industrial plants were placed on stage of alarm, Vietnam Government promulgated specific discharge for wastewater stemming from industries in 1995 (5945-1995). This standard has taken effect from the date of its promulgation. Values of parameters and maximum allowable concentrations of substances in industrial waste waters before being discharged into water bodies are Discharge standards applying for waste waters produced by specific industry such as paper, textile or oil industries are specified in a separate standard, respectively.

Base on comparing and statistic some above standards; we can make some following remarks:

- Compare with the discharge standard of developed countries, concentration of the main pollutants that permitted to directly discharge into commonly stream such as Zn, Cu, Ni, CN, etc. approved in standard of Vietnam 5945-1995 is too low, it is lower 2 times compare with American standard, so not suitable for produce processes and treatment conditions. In addition to, at present, the electroplating industry in Vietnam is relatively small and the weakness of wastes treatment, especially for factories that not joint-venture with foreign organizations.
- Nevertheless, comparing with Discharge standard in Thailand, Vietnam standard is more specific and interested in both the small characteristics and backward of electroplating industry. Hence the constituents and properties of wastewater had been specific assigned by discharge region that give the main different of concentration parameters.

Normally, if standards assign too low, costs for waste treatment will high, that affect on cost price for products, neither it do not stimulate to process produce nor eventually the plant have to stop producing if they do not implement correctly environmental law. Otherwise, if standard proposed too high, it not sure for sustainable development of environment and eco-system, especially affect direct to human health, to animal that wastewater through flow, to population who are living in the area.

Having other affects that Vietnam environmental standard have not mentioned therefore in my opinion should have corporation between management offices, Scientifics and manufacturers in order to give more sensible regulations for sustainable development.

Chapter 2

Methods for analyzing chemical substances

And its application situation in the electroplating industry

Chemical analysis plays a critical role in the successful operation of electroplating processes. Regular chemical analysis of process solution, rinse tanks and effluent streams used in the electroplating industry is essential to the maintaining of product quality. For process solutions, be they those used for cleaning and degreasing, for plating or anodising or for post-treatment such as conversion coatings, the built-up of contaminants or a significant deviation from their specified composition will almost certainly result in coatings which are either obviously defective or whose defects become apparent in subsequent service.

In analytical chemistry of electroplating industry, a large variety of analytical techniques are used, such as:

- Titrimetry (measurement of the volume of a reagent used in a titration).
- Potentionmetry (measurement of the electrode potential due to an ion).
- Thermal analysis (recording of the change in mass on heating).
- Electrochemistry (e.g polarography)

A number of spectroscopic techniques are used for the analysis of materials, such as:

- Atomic absorption spectroscopy (AAS)
- Atomic emission spectroscopy (AES)
- Ultraviolet and visible (UV/Vis) spectroscopy.
- Mass spectroscopy.
- Inductive couple plasma atomic emission spectroscopy (ICP-AES).
- Inductive couple plasma optical emission spectroscopy (ICP-OES).
- Neutron analytical activation

Analytical methods are dependent on the purpose of the analysis, so that it is not possible to use a single method that will be satisfactory for all applications of a substance. A particular method is selected according to the relative importance of the factors-speed, cost and accuracy. Each of these factors assumes a different importance in each application.

2.1. Methods description for chemicals substances analysis

2.1.1. Volumetric (Titrimetric)

Description

In a titration, increments of a reagent solution the titrant are added to the analyte until their reaction is completed. From the quantity of titrant required, the quantity of analyte can be calculated that must have been present. The principle requirements for a titration reaction are to have a large equilibrium constant and to proceed rapidly. Each increment of titrant should be completely and quickly consumed by analyte until the analyte is used up. The most common titrations are based on acid-base, oxidation-reduction, complex formation, or precipitation reactions. The equivalence point occurs when the quantity of added titrant comes up to the exact amount necessary for stoichiometric reaction with the analyte. Actually measured is the end point, which is marked by a sudden change of a physical property, e.g. the electrochemical potential, conductivity, pH, the colour of an indicator (spectrophotometric titration) etc

On the basis that the total amount of added reagent is $C \times V$.

Where:

C = concentration of standard solution

V = volume of standard solution added

It then follows that:

$$C_1 \times V_1 = C_2 \times V_2 \quad (1)$$

Where C_1 and V_1 are concentration and volume respectively of added titrant solution, C_2 and V_2 the same parameters for the solution being analysed.

Since both volumes are known, as is the concentration of the titrant C_1 , these remain only one unknown term and Equation 1 can be solved. Note that no units of the volume or concentration have been mentioned, nor need they be, provided that the same units are used for both values of V and C respectively.

Equipment

The classical titration is carried out by pipetting a known volume of the unknown solution into a conical flask. In more recent years, "automatic" pipettes have become available. Typically these allow the user to dial-up the volume of solution dispensed. Any chipping of the tip of a pipette can affect the accurately of delivered volume.

The conical flask is in effect the "reaction vessel" in which the titration reaction occurs. Good mixing is essential to obtaining a reproducible end-point. The skilled analyst will gently swirl the liquid in the flask during the actual titration. However use of a magnetic stirrer is in every way preferable. Unless otherwise state, titration are carried out at ambient temperature.

There are also more advanced forms of titration which require equipment, e.g. potentiometric titration, thermometric titration etc.

Interferences

Factors affecting accuracy include calibration of the glassware, the volumes used (in general, the larger the better) and the type of indicator or end-point method employed.

The standard solutions used for titrations are often made by dilution of a stock solution. Either these stock solution or the more dilute standard solutions made from them, should be stored for a long time. Loss of water by evaporation (more rarely, gain of water if solution are hygroscopic) will affect accuracy, while many reagent solutions other than the inorganic acids, are liable to undergo chemical change. Alkalis absorb carbon dioxide from the atmosphere, and indeed react with the glass of the bottles in which they are maintained. Chemical decomposition, often promoted by sunlight can also lead to changes in concentration of standard or stock solutions. Any visible change suggests that preparation of a fresh solution is long overdue.

General application: Precise main component analysis of metals (except earth alkali metals), precise determination of stoichiometries and oxidation numbers, determination of concentrations of acids and bases.

In addition this method has also been applying to analyse inorganic ions in plating solution baths of the electroplating industry efficiently.

Detection limit: about 0.1 mg

Relative error: about 0.1 - 1 %

2.1.2 Spectrophotometry (Molecular Absorption Spectrophotometry –UV/VIS)

Description

Spectrophotometry (Colorimetric) is based on the simple relationship between the molecular absorption of UV/VIS radiation by a solution and the concentration of the colored species in solution. The light absorption of the coloured solution is measured at a certain wavelength in the visible or UV spectral range. The absorption is proportional to concentration of the analyse. Concentration of an analyse in solution can be determined by measuring the absorbance at some wavelength and applying the Beer-Lambert Law.

Heavy metals spectrometric methods rely on reactions of analytes with color-forming reagents such as dithizone (for Co, Ni, Zn, Ag, Cd, Hg, Pb, Bi...) and thiocyanates for Ti, Fe(III), Co, Mo, U).

Metal cations which absorb weakly or not at all in the visible spectral region can be changed into strongly colored compounds by means of complexing agents. Strongly colored here means that absorbing bands characteristic of the complex have an extinction coefficient.

The applicable concentration range in ppm is given in the second column (table 2.1)

Table 2.1 Recommended working methods for the photometric determination of some anions and cations in the electroplating water

Units	Concentration Range in ppm	Reagent	λ (nm)
CN ⁻	0.002 - 0.02	Barbituric acid-pyridine	578
NO ₃ ⁻	0.1 - 10	Sodium salicylate	420
NO ₂ ⁻	0.001 - 0.3	Sunfonylamide +N (1-naphthyl-ethylene diamine)	530
SO ₄ ²⁻	2 - 60	BaSO ₄ in solution gelatine (measurement of light scattering)	490
Pb	0.002 - 20	Dithizone	520
Cd	0.002 - 20	Dithizone	530
Cr	0.005 - 10	Diphenylcacbazide	550
Fe	0.01 - 4	1, 10-phenalthroline	510
Cu	0.001 - 0.3	Zn-N,N-dibenzylthiocarbamidate	436
Ni	0.02 - 10	Diacetyldioxime	
Zn	0.004 - 20	Dithizone	530

Instrumentation

The basic components of a spectrophotometer include a light source, a monochromator which isolates the desired source emission line, a sample cell, a detector-readout system and data-processing unit

The light source is usually a hydrogen or deuterium lamp for UV measurements and a tungsten lamp for visible measurements. The wavelengths of these continuous light sources are selected with a wavelength separator such as a prism or grating monochromator. Spectra are obtained by scanning the wavelength separator and quantitative measurements can be made from a spectrum or at a single wavelength.

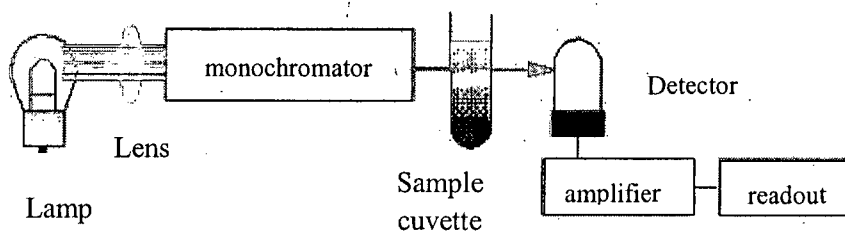


Figure 2.1 Schematic of a single beam UV/VIS spectrophotometer

General application:

UV-VIS spectroscopy is usually applied to molecules and inorganic ions or complexes in solution. The UV/VIS spectra have broad features that are of limited use for sample identification but are very useful for quantitative measurements

Colorimetric methods are often valuable to determine impurities in plating baths with a view to their sensitivity to small amounts of metal.

Detection limit:

About 1 $\mu\text{g/l}$ after preconcentration

Strengths:

- Very easy to use
- Low investment cost
- fast

Limitations

- few interferences
- poor selectivity
- element limitations

2.1.3. Flame atomic Adsorption Spectroscopy (FAAS)**Description**

AAS involves the absorption of radiant energy produced by a special radiation source, by atoms in their electronic ground state. The lamp emits the atomic spectrum of the analyte elements, just the energy that can be absorbed in a resonance manner. The analyte elements are transformed in atoms in an atomizer. When light passes through the atom cloud, the atoms absorb ultraviolet or visible light and make transitions to higher electronic energy levels. A monochromator is used for selecting only one of the characteristic wavelengths of the element being determined, and a detector, generally a photomultiplier tube, measures the amount of absorption. The amount of light absorbed indicates the amount of analyte initially present.

Analyse solution is sprayed as an aerosol either into a flame (oxygen-acetylene or nitrous oxide-oxygen) or into an electrically heated graphite furnace. At temperatures between 2400 and 3100 K the sample is vaporized and atomized. Light of a certain wavelength is passed through the flame/furnace and is adsorbed by the atomized analyte element. The required wavelength that can be adsorbed by the atomized element is emitted from a hollow-cathode lamp made from the element that has to be analyzed. Atomic absorption spectrometry is the most widely used techniques for heavy metals quantitative analysis in environmental samples and the plating industry.

Instrumentation

There are five basic components of an atomic absorption instrument:

- The light source that emits the spectrum of the element of interest.
- An "absorption cell" in which atoms of the sample are produced
- A monochromator for light dispersion.
- A detector, which measures the light intensity and amplifies the signal.
- A display that shows the reading after it has been processed by the instrument electronics.

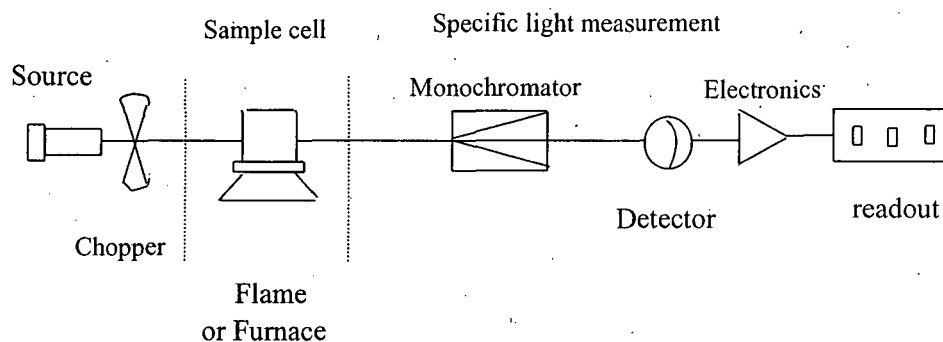


Figure 2.2. Single-beam atomic absorption Spectrometer

General application:

Precise main component analysis of metals (except earth alkali metals), precise determination of stoichiometries and oxidation numbers, determination of concentrations of acids and bases.

Detection limits: < 10 µg/l for Li, Be, Na, Mg, K, Ca, Mn, Cu, Zn, Ag, Cd

10 -100 µg/l for Al, Ti, V, Fe, Co, Ni, As, Rb, Sr, Rh, Te, Cs, Au, Ti, Pb

100-100 µg/l for Si, Sc, Cr, Ga, Ge, Se, Y, Ru, In, Sn, Sb, Ba, Ta, Os,

Pt, Hg, Bi

Strengths

- Easy to use
- Very fast
- Low capital cost
- Relatively few interferences
- Very compact instrument
- Good performance
- Robust interface

Limitations

- Moderate detection limits
- Element limitations
- 1-10 elements per determination
- No screening ability

2.1.4. Graphite furnace atomic absorption Spectrometry (GFAAS)

Description

This technique is essentially the same as flame AA, except the flame is replaced by a small, electrically heated graphite tube, or cuvette, which is heated to a temperature up to 3000°C to generate the cloud of atoms. The higher atom density and longer residence time in the tube improve furnace AAS detection limits by a factor of up to 1000x compared to flame AAS, down to the sub-ppb range. However, because of the temperature limitation and the use of graphite cuvettes, refractory element performance is still somewhat limited.

Numerous metals can be analyzed by GFAA, as long as their atoms can be vaporized in the graphite furnace. Such elements include aluminum, arsenic, barium, boron, cadmium, calcium, chromium, cobalt, copper, iron, lead, lithium, magnesium, manganese, mercury, molybdenum, nickel, potassium, selenium, silicon, silver, sodium, titanium, terbium, vanadium, ytterbium, and zinc.

Detection limits

Detection limits can be very low with GFAA analyses (below most of the maximum contaminant levels for drinking water established by the U.S. Environmental Protection Agency (EPA) and usually are 10 to 100 times lower than the detection limits for analyses by flame AA or ICP for the same element.

0.01 µg/l for Be, Mg, K, Cr, Mn, Fe, Cu, Co, Zn, Sr,
Ag, Cd

0.01 - 0.1 µg/l for Li, Na, Al, Ca, Sc, Ni, Ga, Rb,
Mo, In, Cs, Ba, Au, Ti, Pb, Bi

0.1-0.5 µg/l for B, Si, Ti, V, Te, Ge, As, Se, Y, Zr,
Nb, Tc, Ru, Rh, Pd, Sn, Sb, Hg..

Strengths

- Very good detection limits
- Small sample volume
- Moderate price
- Very compact instrument
- Few spectral interferences

Limitations

- Slower analysis time
- Chemical interferences
- Element limitations
- 1-6 elements per determination
- No screening ability
- Limited dynamic range

2.1.5. Atomic emission spectroscopy (AES or ICP-OES)

Description

Atomic emission spectroscopy (AES or OES) uses quantitative measurement of the optical emission from excited atoms to determine analyte concentration. Analyte atoms in solution are aspirated into the excitation region where they are desolvated, vaporized, and atomized by a flame, discharge, or plasma. These high-temperature atomization sources provide sufficient energy to promote the atoms into high energy levels. The atoms decay back to lower levels by emitting light. Since the transitions are between distinct atomic energy levels, the emission lines in the spectra are narrow. The spectra of multi-elemental samples can be very congested, and spectral separation of nearby atomic transitions requires a high-resolution spectrometer. Since all atoms in a sample are excited simultaneously, they can be detected simultaneously

Plasma (gaseous mixture containing cations and electrons) is used as the atomization excitation source (see figure 2.3)

- Very high temperature : 8000 - 10,000 K
- Can determine multiple elements in the same sample.
- Three types - simultaneous PMT (photo multiplier tube) spectrometer, sequential PMT spectrometer, and charge injection device (CID) spectrometer.

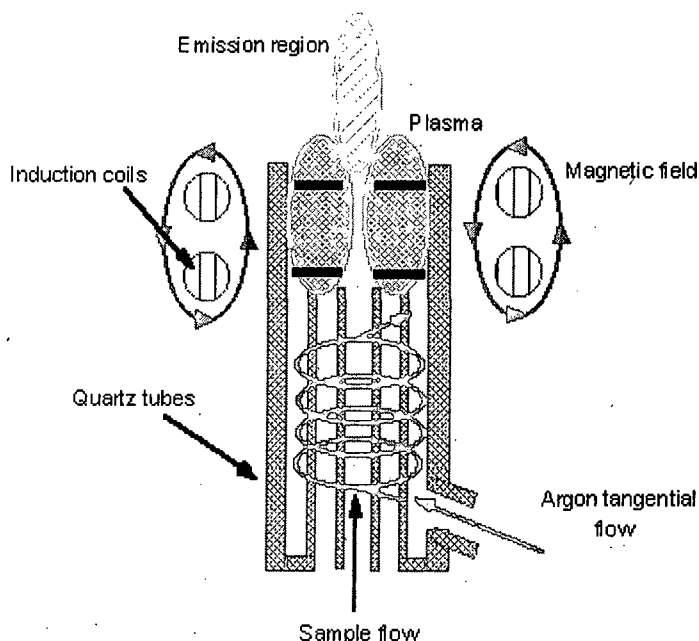


Figure 2.3. Plasma source

Instrumentation

The apparatus for the ICP-OES (AES) is composed of the main sections: the torch, monochromator and the detection system, readout device (Figure 2.4).

1. **Argon plasma torch** - very high and uniform temperature, long residence time result in linear response over large concentration range
2. **Monochromator** (Sequential PMT) or **polychromator** (simultaneous PMT)

3. **Detector(s): PMT** - measure only one specific wave length at a time, **CID** - quantitative determination of the intensity of every spectral line in the emission

4. **Readout device**

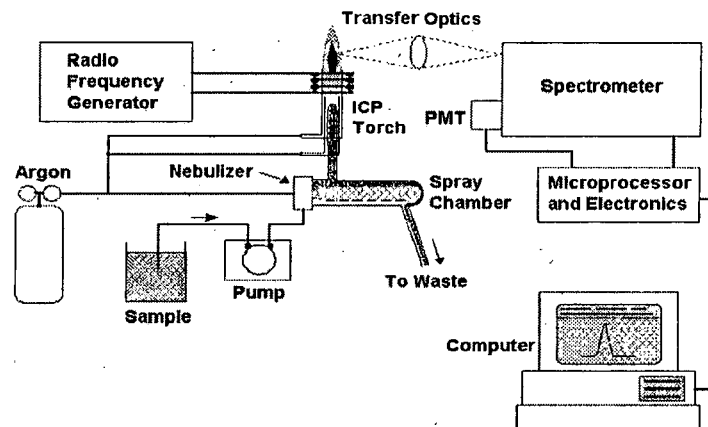


Figure 2.4 ICP-OES (AES) schematic diagram

Detection limits: 0.1 – 10 $\mu\text{g/g}$ (solids), 1 – 50 $\mu\text{g/l}$ (aqueous)

Strengths

- Easy to use
- Multi-element
- High productivity
- Very economical for many samples and/or elements
- Few chemical interferences
- Robust interface
- Excellent screening abilities
- High total dissolved solids
- Solid and organic samples

Limitations

- Moderate to low detection limits (but often much better than FAAS)
- Spectral interferences possible
- Some element limitations

2.1.6. Inductively coupled plasma mass spectrometry (ICP-MS)

Description

The elements are ionized in the plasma flame of an argon plasma and analyzed by a high resolution mass spectrometer. Methods of sample introduction into the flame are a nebulizer for liquid samples or laser ablation for solid samples. The sample, which must be in a liquid form, is pumped at 1 ml/min (usually with a peristaltic pump) into a nebulizer, where it is converted into a fine aerosol with argon gas at about 1 L/min. The fine droplets of the aerosol, which represent only 1 - 2% of the sample, are separated from larger droplets using a spray chamber. The fine aerosol then emerges from the exit tube of the spray chamber and is transported into the plasma torch via a sample injector.

ICP-MS is a multi-element technique that also uses an ICP plasma source to dissociate the sample into its constituent atoms or ions. However, in this case, the ions themselves are detected, rather than the light that they emit. The ions are extracted from the plasma and passed into the mass spectrometer, where they are separated based on their atomic mass to charge ratio by quadrupole or magnetic sector analyzer.

The high number of ions produced, combined with very low backgrounds, provides the best detection limits available for most elements.

Quadrupole mass spectrometers are most common in ICP-MS but magnetic sector instrumentation fulfils exacting requirements that demand the ultimate detectability and isotope ratio measurement. Magnetic mass analyzer are more expensive, less common and less easy to operate than quadrupoles.

Instrumentation

ICP-MS includes nebulizer, spray chamber, plasma torch, interface, and detector but can differ significantly in the design of the mass spectrometer and in particular the mass separation device. Figure 2.5 shows the basic instrumental components that make up an ICP-MS system.

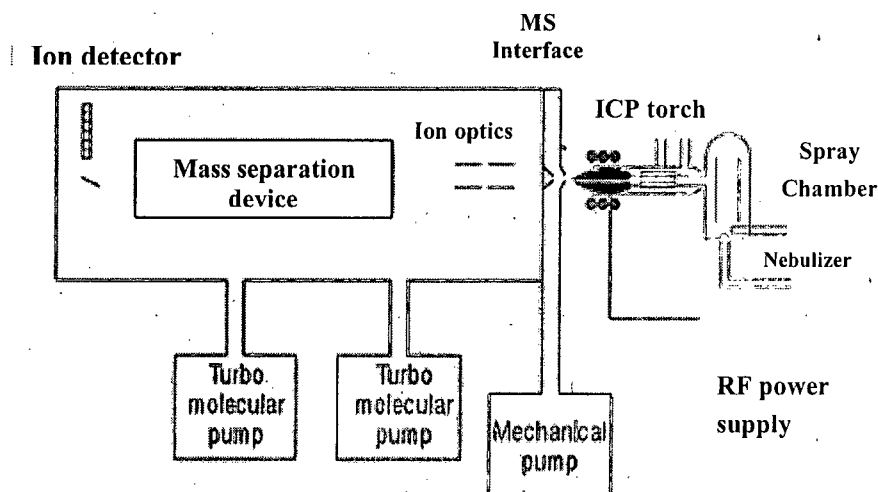


Figure 2.5. Basic instrumental components of ICP-MS

Detection limits: Quadrupole 1-10 ng/l, magnetic sector 0.01-0.1 ng/l

Strengths

- Excellent detection limits
- Multi-element
- High productivity
- Very economical for many samples and/or elements
- Wide dynamic range
- Isotopic measurements
- Fast semiquantitative screening
- Hybrid techniques
- Easily interpreted spectra

Limitations

- Some method development skill required
- Higher initial capital cost
- Some spectral interferences, but well defined
- Limited to <0.2% dissolved solids

2.1.7. Other methods

2.1.7.1. Electrochemical methods

Description

Electroanalysis is a broad spectrum of techniques that can be distinguished by the variable that is controlled: voltage or current. The usual practice is to apply one of these variables to a solution containing the analyte species and measure one of the other variables. From a plot of the measured variable versus the applied variable, information regarding the concentration and identify of electroactive species in solution is determined. Of the many electrochemical techniques, only a few are routinely used for environmental analysis: voltametry, direct-current, polarography, and potentionmetry.

Voltametry is the name usually given to the family of techniques in which current is measured in function of applied potential. Anodic stripping voltammetry (ASV) is used for the determination of metals in soils and water. The measurement is performed in an electrochemical cell under polarizing conditions on a working electrode. Analysis includes a two step process consisting of electrolysis and stripping. The analyte of interest is reduced and collected at the working electrode, the stripped off and measured. Electroanalytical techniques can provide quantitative and qualitative information. They are also among the most cost effective methods to do environmental analysis.

Detection limits: 1 – 50 µg/l

Environmental applications: electrochemical determination of metal ions has been widely applied to seawater, natural and potable water, wastewater sewage and other matrices. Electrochemical techniques are able to determine most transition metals and metalloids. The polarograph is an instrument that measures the voltage and amperage characteristics of a dropping mercury electrode. It has been applied to the rapid simultaneous determination of copper and zinc in brass deposits. It is obvious that this instrument can be used for determination of the metal content of most the plating baths.

2.1.7.2. Gravimetric methods

Description

Formerly very widely used, but now are not used for plating bath control because they are slower than the other types of methods. The gravimetric methods consist of careful separation of a chemical compound from other substances in the bath. The compound is precipitated, washed, dried and weighed. These methods require a balance and an oven, depending on the drying step. The gravimetric methods are generally accurate and are often used for check work where a substance is determined by more than one method.

Detection limit: about 5 mg

Relative error: 1 % or below

2.1.7.3. Electrolytic methods

Electrolytic methods may come under the general classification of gravimetric methods because the metal is weighed. In the electrolytic methods, the metal sought is deposited on a platinum cathode. It is washed, dried, and weighed. These methods are usually faster than the other gravimetric methods and are quite accurate. The high accuracy can be obtained is indicated by the fact that the electric current is standardized in terms of plating silver from a silver nitrate solution.

2.1.7.4. Ion chromatography (IC)

IC is a form of liquid chromatography that uses ion exchange resins to separate atomic and molecular ions based on their interaction in the resin. It is most convenient analytical approach for the determination of environmentally important inorganic anions such as: NO_3^- , NO_2^- , PO_4^{3-} ... However, it has gained in importance for metal determination. For cation separation, the cation exchange resin is usually a quaternary ammonium group. Metals in solution are generally detected by measuring the conductivity of the solution. Post column reactions can be employed to enhance the specificity and selectivity of the detection.

The lack of selectivity control limits the versatility of IC methods, particularly if there is interest in trace metals eluting in the presence of massive amounts of other metals.

However, there is a solution to this problem, that is, to use a metal chelating ion-exchange rather than a simple ion exchange substrate.

Detection limits: 1-50 µg/l

Environmental applications: Although IC can be used for the direct determination of some heavy metals, it is more often combined with atomic spectrometry for metal speciation analysis.

2.1.7.5. Neutron activation analysis (NAA)

NAA is a highly sensitive procedure for determining the concentration of chemical elements in the most varied substances. NAA is based on conversion of stable nuclei of atoms into radioactive ones and subsequent measurement of characteristic nuclear radiation emitted by the radioactive nuclei. When a nuclear reaction results at a radioactive nucleus, the process is denoted by various means. The produced radionuclide decays to a stable atomic nucleus under emission of characteristic radiation. By determination the energy of the gamma-radiation and using the decay schemes, the emitting radionuclide can be identified as well as the nature of the activated element. Quantitative activation analysis is based on measurement of the intensity of the radiation. The radioactivity is proportional to the number of target nuclei in the irradiated sample. The main drawback of NAA is probably the high cost and limited access to the facilities.

When the sensitivity of instrument activation analysis is insufficient, radiochemical neutron activation analysis may be used. In this case, the radioirradiation corresponding to the elements of interest are chemically separated postirradiation. Various separation techniques can be used including ion exchange, chromatography, precipitation, electrolysis, and distillation. The separation schemes are specific not only for the elements to be measured, but also for the matrix composition of the material.

Detection limits: depending upon the kind of material under investigation the limits of detection may be as low as 0.1 ng/g.

Environmental applications: NAA can be performed for a number of heavy metals by measuring the gamma activities of their activated radioisotopes.

2.2. Application status of substances chemical analysis in the electroplating industry

Nowadays, in the world, analysis problems in the electroplating industry for chemical substances are considering very important and critical. It is an essential partially and primary of implementing EMS and QMS system.

A company want to have better products, higher competition ability and can be met requirements of customer in about product' quality and environment hence have to employ monitoring and analysis frequently, comply with standard processes.

Switzerland has about 300 electroplating companies and approximate 50% of these companies have a laboratory for analysis in baths and effluents.

- For solutions in the bath: Predominantly companies have still used titration methods. In other hand, some companies are assured by chemical supplier. Time for implement depend on quality of elements and ions in the solution.
- For checking water' quality after treatment, Switzerland electroplating companies use different instruments. They can use FAAS, colorimetric, curvet test or by indicator papers that can determine quickly. If water reaches to discharge standard, they can be released into public drainage to treat appropriately.
- A lot of companies send samples to professional laboratory

Until now, the supply houses play a pivotal role in the continuing viability of the plating industry in Switzerland, particularly for the very small companies. Not only do they supply chemical solutions for plating and reagents/methods for analysis, they also offer analytical services to their clients. They maintain laboratory facilities containing a wide range of sophisticated instrumentation and staff trained to solve their customers' problems

USA: Total number of companies surveyed: 45 in which 95,6 % companies support an in-house laboratory used for routine analysis of plating solution to ensure that solution composition is maintained within optimum operating values.

Of the 43 in-house laboratories, 93% reported the use of titrimetric methods of analysis. 41.9% had access to a supporting instrumental technique, commonly atomic absorption spectroscopy and (4.7%) had access to two or more instrumental techniques to support trace metal analysis or other analytical investigations. (79.1%) reported their titrimetric procedures originated from their supply house in accordance with the use of proprietary plating solutions. Other methods used were considered standard trade methods, (44.2%), and (9.3%) had developed their own in-house methods, primarily to support instrumental analysis.

(74.4%) of the laboratories used cross referencing against results obtained from the supply house as a method of monitoring analytical data, but not always on a regular basis. In-house routine analysis is generally on a regular weekly basis dependent upon solution use and performance, though more frequent daily analysis is needed for autocatalytic processes involving continuous depletion. Most (79.1%) of the in-house laboratories purchase prepared standard solutions from chemical suppliers to support their titrimetric analysis

The analytical techniques used by the small companies are essentially titrimetric, the procedures followed being provided by either the supply house or obtained from standard reference texts. Instrumental procedures are commonly used by the larger plating companies, who by the nature of the volume and diversity of their work can justify the investment in these newer technologies.

The use of modern instrumental procedures (mostly spectroscopic) appears to be restricted to the larger plating companies and the supply house laboratories. This is to be expected

given the high cost of the instrumentation and the skill required both using and maintaining the equipment.

Vietnam: A few companies have laboratories but instruments are very rudimentary and less work frequently. Water quality after treatment have almost uncontrolled. For some big companies, they can send samples to labs in universities or institutes but not very often.

Predominantly, electroplating companies data about wastewater that were get from Environmental assessment impact reports or government' projects which implemented and supported by financial from government. Electroplating companies have virtually not approached with analytical methods and have not identified obviously benefits of analyzing.

All data have just had typical characteristics, unreliability. In fact, most of the electroplating companies in Vietnam have still not analyzed and monitored wastewater after treatment.

Checking quality of bath solutions, some companies are also using titration methods, but not much and infrequent. At the moment, Hanoi has 2 environmental monitoring and pollution control centrals. Every year, these centrals only implement at some typical companies and not frequently. The collected samples have only analyzed simple parameters whereas heavy metals and organic parameters do not significantly mention due to costs for analyzing is still expensive and financial sources limited.

These central often take samples and measure quick parameters then samples will be sent to laboratory of University or institute laboratories to analyze.

For monitoring centrals and lab of universities (INEST) have lot difficulties in analyzing and measuring frequently such us:

- Analytical expenditure
- Standard processes and standard methods to determine
- Lack of management policies for implementing efficiently
- Identify what instrument is effective and
- How to analyze efficiency.
- How long they can be monitored.
- How to combine closely with electroplating companies.

Likewise, have not regulations and management tools properly for monitoring central, laboratories in Universities. Companies have not standard methods and obligatory regulations to implement. Choosing and suggesting analytical methods appropriate for Vietnam electroplating industry will be given in chapter 5.

Parallel with applying of analytical methods in electroplating industry, effluent control also a good methods to pollution prevention, recovery and recycle wastes efficiently. The Effluent control methods will give in follow chapter.

Chapter 3

Pollution prevention and effluent control Technologies in the electroplating industry worldwide and in Vietnam

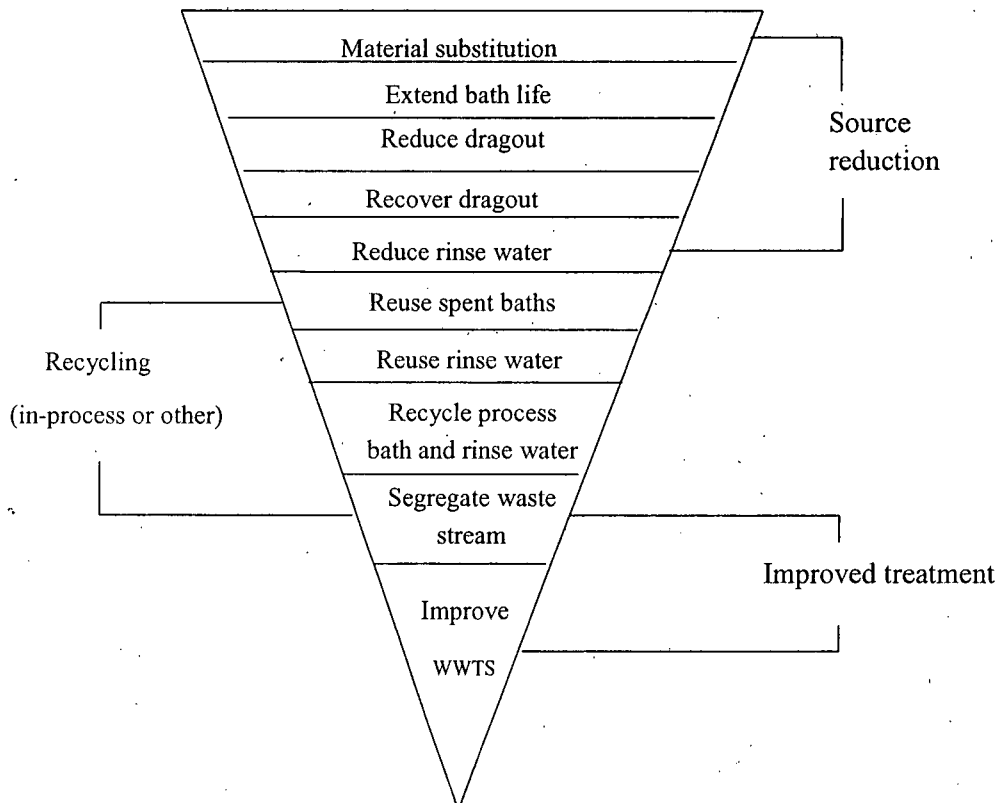
3.1. Effluent control methods and pollution prevention that have applied worldwide

Environmental solutions for electroplating industry include the reduction and control of wastes generated by the industry. This waste reduction and control approach integrates the concepts of pollution prevention and waste management control technologies.

Pollution prevention focuses on product and process changes that reduce the volume and toxicity of production wastes and the reduction of end-product wastes during the product lifecycle. When waste cannot be reduced by pollution prevention methods, the preferred alternatives are recovery/reuse/recycle of the process materials during the lifecycle of the product. Where prevention or recycling are not feasible, waste treatment followed by authorized disposal is required to achieve environmental compliance.

“End-of-pipe” approaches were the earlier methods for achieving environmental compliance, controlling releases and environmental clean-up. These approaches not only can be expensive, they often transferred pollution from one media to another.

Hierarchy of pollution prevention and waste management strategies for electroplating industry are given as following:



Today's trend is to integrate the best practices and technologies available to meet the goals of industry and environmental regulations.

3.1.1 Recovery, Recycle and Extended Bath Life

The most common pollution prevention option for electroplating being implemented today is reusing the drag-out rinse water. This involves using the tank water where the parts have been rinsed to replace the process tank water lost through evaporation.

This reuse of drag-out rinse water reduces chemical loss. Other waste rinse water pollution prevention alternatives include:

- Operate equipment to reduce drag-out;
- Increase solution temperature;
- Lower the concentration of plating bath constituents;
- Reduce speed of product withdrawal to allow for drainage time;
- Use surfactants to lower solution surface tension;
- Position part properly on rack for maximum drainage;
- Use multiple rinse tanks in counter current series;
- Use fog nozzles and sprays for rinsing simple work pieces;
- When still-rinsing, recycle rinse water upstream
- Use automatic flow instrumentation to control flow rate;
- Reuse rinse water when possible;
- Increase rinsing efficiency by agitating rinse bath.

Pollution prevention alternatives for work cleaning wastes are:

- Reduce cleaning frequency when possible;
- Design process and equipment to minimize surface area of exposed process liquid;
- Convert from a batch process to a continuous process;
- Maximize dedication of process equipment;
- Avoid unnecessary clean-ups;
- Operate equipment to inhibit fouling;
- Minimize residue build-up during operation;
- Minimize the amount of cleaning solution used;
- Recycle cleaning solution by filtering solids from used solution;
- Substitute cleaning system with a proprietary process

Pollution prevention alternatives for waste treatment include:

- Install a sludge dewatering system;
- Improve operating practices;
- Install a metal recovery system;
- Segregate waste streams to facilitate treatment and recovery of metals;
- Use the most efficient precipitating agents;

There are a number of control effluent technologies that electroplater can use. By using the following technologies, finishers can practice cost-effective and environmentally friendly resource recovery in several ways:

1. Recover the process solution and directly add back into the process tank.
2. Remove contaminants from process solutions to greatly extend solution life.
3. Recover metals that can be reused or sent back to suppliers.

Control technologies that are used within electroplating industry to separate plating chemicals from rinse waters, or to concentrate the chemicals for ease of recycle/reuse. The six most commonly used technologies are:

1. Electrowinning
2. Atmospheric Evaporation
3. Vacuum Evaporation
4. Ion Exchange
5. Reverse Osmosis
6. Electrodialysis

3.1.1.1. Electrowinning

Electrowinning involves placing two electrodes (insoluble anode and cathode) in a solution containing ions, where there occurs a movement of ions toward the charged electrodes. Dissolved metals in the electrolyte are reduced and deposited on the cathode. The deposited metal is removed by mechanical or chemical means and either reused as anode material or sent off-site for processing or disposal. Electrowinning is used to recover valuable common metals for recovery/reuse or to reduce the amount of inexpensive metals for treatment and disposal. This technology is most often applied for gross metal recovery from concentrated solutions. The combination of ion exchange and electrowinning has much higher potential metal recovery efficiency than electrowinning from a dragout rinse.

Electrowinning is inexpensive to operate and not labour-intensive. Energy costs comprise only a small part of the total operating costs.

Often electrowinning is combined with ion exchange to recover metals (see Figure 3.1). Ion exchange processes a large volume of dilute rinse water and concentrates the metals. The regenerate flow is pumped to the recovery cell. Electrowinning can recover 90-95% of the available metals.

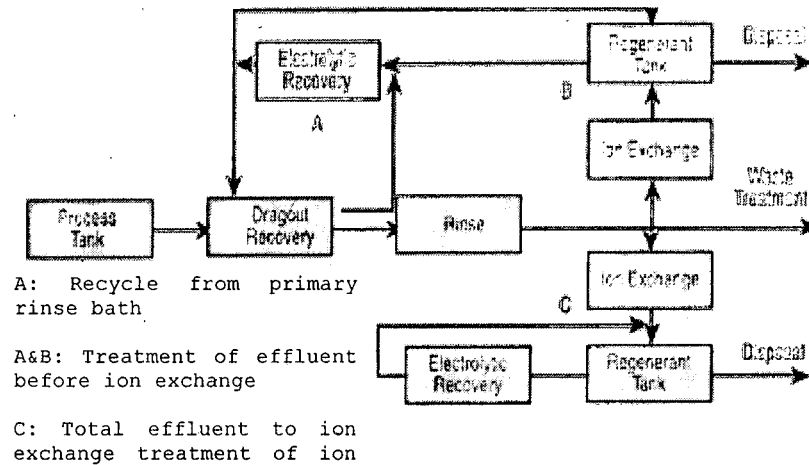


Figure 3.1 Electrowinning is often combined with ion exchange

Advantages:

- Recovers metal only
- Results in salable, nonhazardous product.
- Energy efficient
- Low maintenance

Disadvantages:

- Solution concentration must be monitored.
- Fumes may form and may require hood scrubbing system
- Solution heating encouraged to maximize efficiency

3.1.1.2. *Atmospheric evaporation* is used to concentrate liquid plating wastes prior to treatment/storage/disposal. This technology reduces the amount of waste and consequently lowers costs for transportation, treatment, storage and disposal. Atmospheric evaporation is the most widely used method for chemical recovery in the plating industry. An evaporator is a device that evaporates water to the atmosphere and incorporates a pump for moving the solution, blower to move the air, heat source, mixing chamber for mixing the solution and air and mist eliminator to remove any entrained liquid from the exhaust air stream. The capital and operating costs can be relatively low in some installations in arid climates.

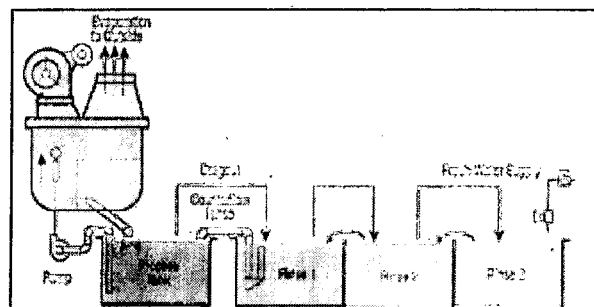


Figure 3.2 Atmospheric evaporation

Advantages:

- Established and proven technology, very reliable.
- Simple to operate
- Widely applicable
- Can exceed bath concentration.

Disadvantages:

- Some units are energy intensive.
- Multi-stage counter rinsing
- Returns bath with impurities.
- Additional treatment may be needed control impurities.
- May requires pH control

3.1.1.3. Vacuum evaporation systems are relatively complex and more expensive than the simpler atmospheric evaporation systems. The vacuum evaporator is a distilling device that vaporizes water at low temperature when placed under a vacuum. In the system shown in Figure 3.3, a vacuum pump draws rinse water that contains dragged-out process chemicals from selected rinse tanks through the system.

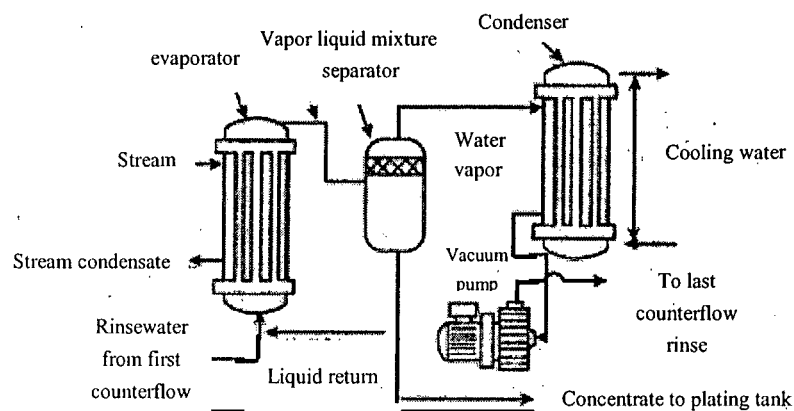


Figure 3.3 Vacuum evaporation, climbing-film type

One of the drawbacks for vacuum evaporation is its high capital and operating costs. However, it has found a niche in evaporating process solutions that have heat sensitive compounds.

Vacuum evaporators consume high qualities of energy, making the technology less comparative on an operational cost basis.

4. Ion exchange

Ion exchange is a chemical reaction recovery technology that is especially applicable to dilute rinsewaters. It involves exchange of the ions from a plating solution with similarly charged ion attached to an immobile solid particle, such as an ion exchange resin. The resins are typically contained in vessels (columns), and the exchange occurs when the solution is passed through these columns. A simple diagram illustrating the use of the ion exchange method is presented in Figure 3.4.

Ion exchange is not practical for process solutions that are more concentrated than the ion exchange regenerate; therefore, this technology does not work well for concentrated drag-out solutions. The capital and operating costs can be relatively high for the benefits received from nickel chemicals.

Regeneration of ion exchange columns depends on the type of column. If the column is cationic, acid is used. Here acid flows through the bed, exchanging its hydrogen ions for the metallic ions. Anionic columns are regenerated in a similar fashion using sodium hydroxide. Here, the sodium hydroxide flows through the bed, exchanging its hydroxyl ions for the negatively charged ions

Depending on the conditions, the regenerate solution can be directly returned to the process tank or undergo further reclamation or treatment.

Advantages:

- Low energy demand
- Handles dilute feed
- Returns metal as metal salt solution

Disadvantages

- Requires tight operation and maintenance equipment complex.
- Limited concentration ability.
- May require evaporation to increase concentration.
- Excess regenerate must be closely monitored.

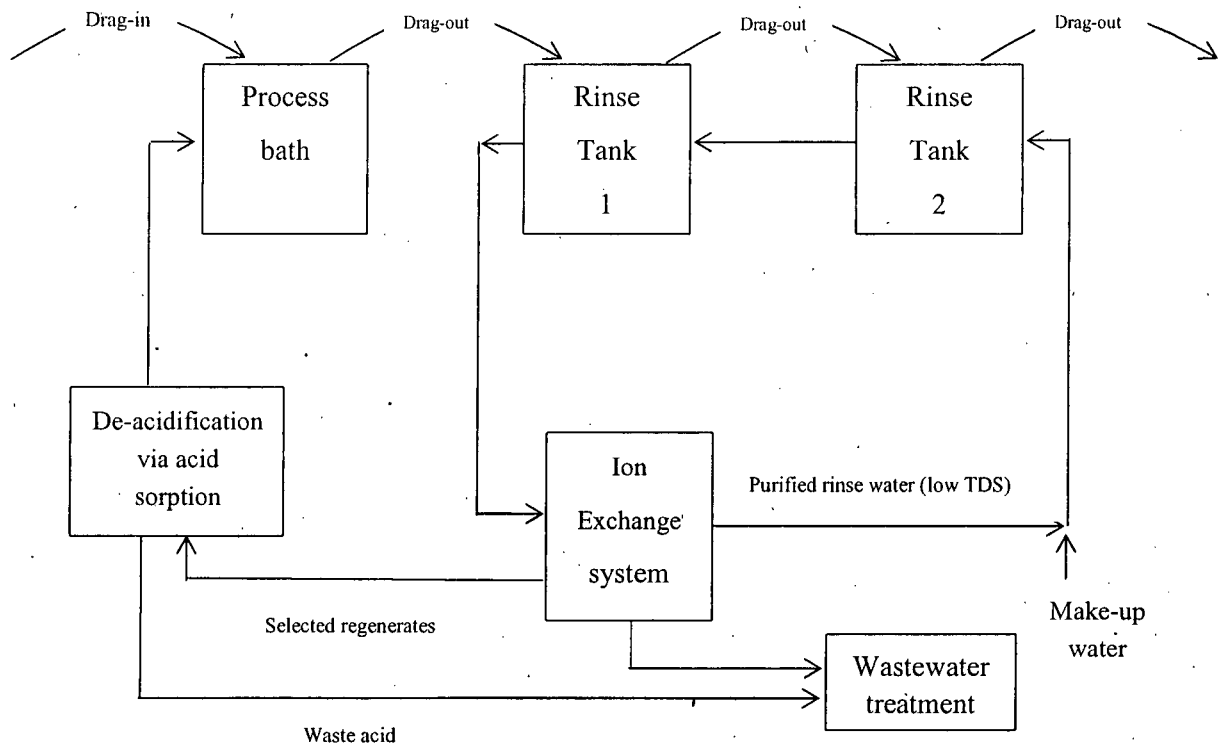


Figure 3.4 Ion exchange flow diagram

3.1.1.5. Reverse osmosis (RO)

RO is a membrane separation technique applicable to dilute streams. RO is used primarily to separate water from a feed stream containing inorganic ions. The purity of the recovered water is relatively high and the water is generally suitable for recycling.

Osmosis occurs when a semi-permeable membrane separates two solutions of different dissolved-solids concentration. Pure water (permeate) will flow through the membrane into the concentrated solution, while rejected ions (brine) are retained behind the membrane. RO occurs when pressure is applied to the more concentrated solution to reverse the normal osmotic flow, with the pure water forced through the semipermeable membrane into a less concentrated solution. The purified stream that passes through the membrane is called permeate; the concentrated stream retained by the membrane is called concentrate. Chemical recovery by RO is usually not practical for highly concentrated, oxidative solutions, due to fouling. A typical RO application is shown in Figure 3.5

Ro system have been used to recover chromium, copper, zinc, brass, cadmium, tin, palladium and other precious metals, but the most common application for RO technology is recover of acid nickel.

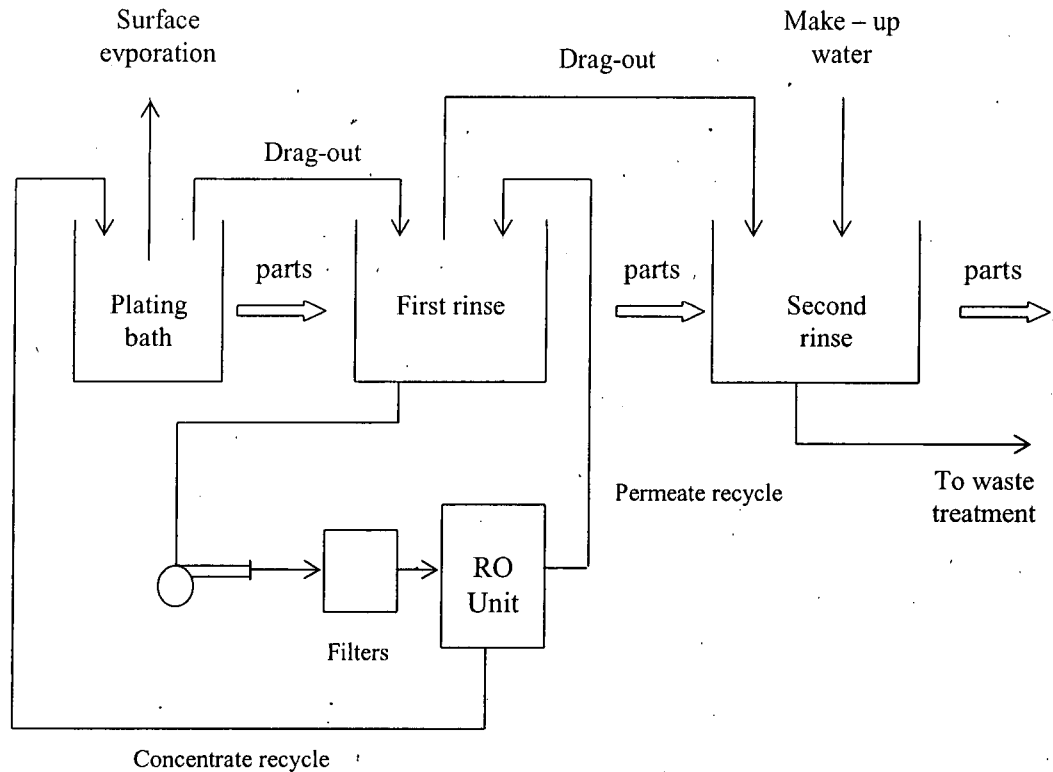


Figure 3.5 Typical reverse osmosis system

Advantages:

- Achieves modest concentration
- Small floor space requirement
- Less energy intensive than evaporation

Disadvantages

- Limited concentration range of evaporation .
- Fouling of membrane due to high level of suspended solids in feed solution, feed filtration essential.
- Membrane sensitive to pH.
- Some materials fractionally rejected.
- May require further concentration.

3.1.16. Electrodialysis (ED)

Electrodialysis is a proven recovery technology that uses membranes and direct electrical current to concentrate and separate ionic contaminants found in rinse water.

The rinse water is passed through a series of alternately placed cation and anion permeable membranes across which there is an electropotential charge (see Figure 3.6). The cationic

exchange membranes allow only the positively charged ions, such as nickel, copper and zinc, to pass through. Anionic exchange membranes allow only negatively charged ions, such as sulfate, chloride or cyanide, to pass through.

Because of the alternating arrangement and electropotential, a concentrated stream and purified stream are produced. The concentrated solution is returned to the plating tank while the purified stream is returned to the rinse tank.

ED technology has been successfully applied to a number of acids, alkaline and cyanide based plating solutions but has been most successful in recovering chromates, tin, nickel, gold and silver. Also, ED has been effective as a "roughing" treatment before reverse osmosis or ion exchange for water with a very high total dissolved solids content

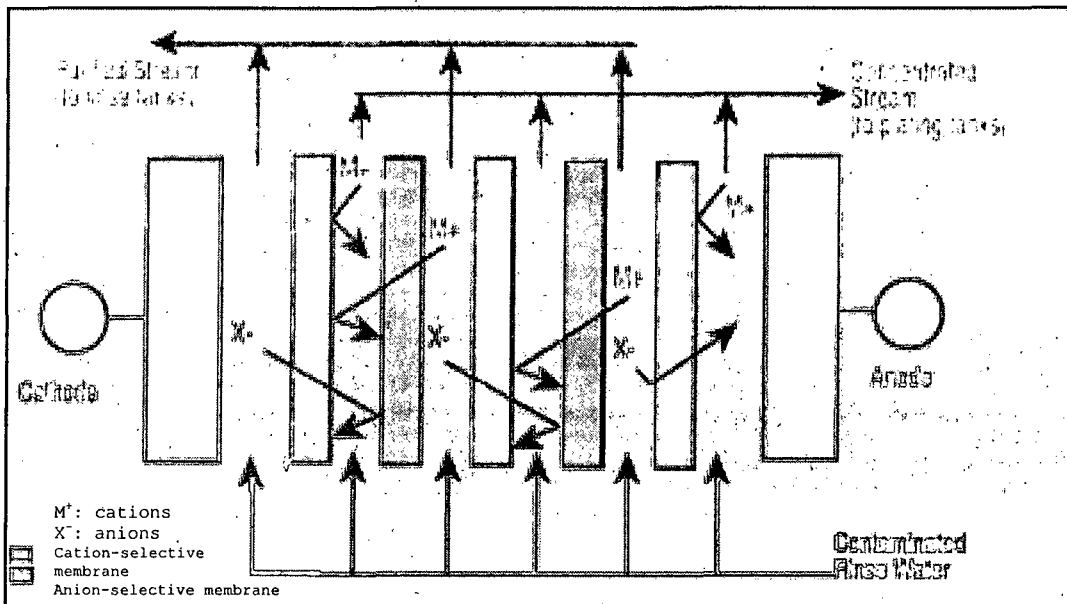


Figure 3.6 Electrodialysis schematic diagram

Advantages:

- Achieves higher concentration than reverse osmosis or ion exchange.
- Energy efficient.
- Organic not concentrated.

Disadvantages

- Feed must be filtered.
- Membrane sensitive to flow distribution, pH and suspended solids.
- Equipment uses multi-cell stacks, incurs leakage.
- Chemical adjustment of recovered material.
- Membrane life uncertain

After minimizing water use by rinsewater reduction or reuse and metal recycling, the focus for pollution prevention is on extended bath life. An appropriate method to conserve water and conserve chemicals while maintaining bath life is a closed-loop plating bath

recycling system. Figure 3.7 shows how a closed-loop plating bath recycling system can be arranged to extend bath life.

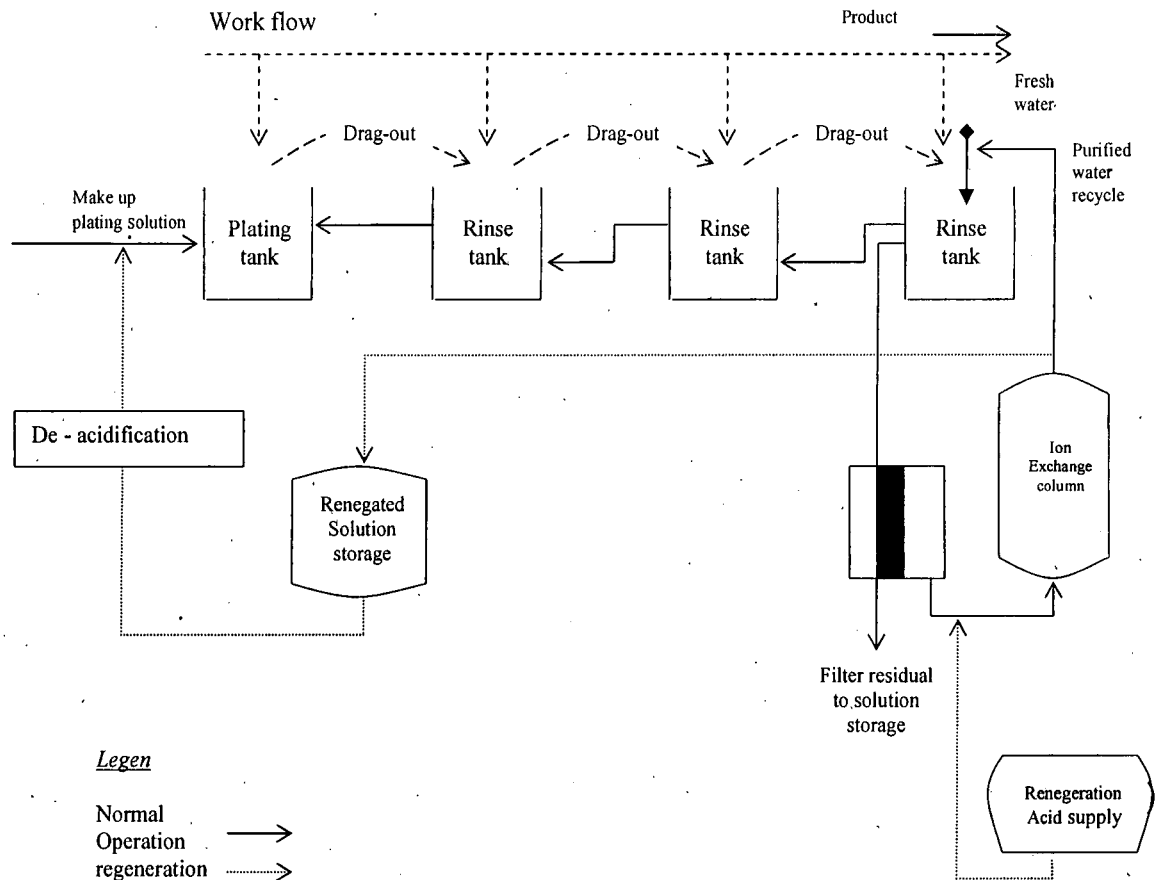


Figure 3.7 Closed loop progress flow diagram for bath life extension

Another method to extend plating baths is to remove contaminants, such as grease, oil, organic impurities from proprietary additives, and unwanted metals from the metal baths. The most common treatment technologies used are electrolytic treatment), batch metal precipitation, and batch adsorption.

Carbon adsorption is an effective method for removing specific organic contaminants from plating baths.

Water used for evaporation loss can be a major source of contaminants. Therefore, de-ionized water should be used for solution make-up. Continuous or batch filtration through activated carbon is recommended to eliminate decomposition products and minor levels of oils and greases that may be dragged into the baths. These purification methods can be combined for greater contamination removal.

Removing contaminants to extend bath life can reduce costs by reducing process chemicals, energy usage, quantities of wastes for treatment/disposal and the potential for noncompliance. Plating bath solution maintenance has become a greater priority to plating shops for extending bath life and improving the operating efficiency and effectiveness of a plating solution.

3.1.2 Process Changes

Changes can be made in the production process through improved operation and maintenance procedures, material substitutions, or changes in equipment that will reduce waste generation. Operating the plating line more efficiently can reduce waste generation and is usually inexpensive to implement. Instituting standard operating procedures and optimizing the use of raw materials can increase overall efficiency.

Material substitution is a more difficult means for reducing waste generation because it may require product reformulation with a less hazardous or non-hazardous material, that may adversely impact quality.

Examples:

- Using water-based cleaning systems instead of solvent, and replacing chlorinated solvents with nonchlorinated solvents.
- Adding more holes to a product or designing product shape for better drainage or easier shipping may also reduce waste and costs.
- Redesigning a fixture to allow better escape of gases generated on the plating surface may reduce the waste of plating chemicals.

3.1.3 Life Cycle and Sustainability Considerations

While the major focus of environmental impacts occurs within the manufacturing stage for metal platers, life-cycle assessment (LCA) utilizes a comprehensive approach by analyzing the entire product life cycle. This approach is comprised of four stages:

- Raw materials acquisition;
- Manufacturing;
- Use/reuse/maintenance; and,
- Recycle/ waste management.

LCA is a systematic method for identifying, evaluating, and minimizing the environmental consequences of resource usage and environmental releases associated with a product, process, or package.

LCA evaluates the mass, energy inputs, and product outputs for an industrial system in an effort to identify their possible environmental significance. The life-cycle impact assessment goes beyond the unit operation to encompass a cradle-to-grave perspective. The purpose of using LCA is to avoid shifting pollution from one media to another or from one life cycle stage to another.

LCA can bring benefit companies that want to strategically evaluate their position on environmental impacts in reference to the rest of the industry. The life cycle concept can be employed for any product, process or design activity. LCA can be used as a screening tool to help the user determine if impacts occur outside the facility when an improvement is made to the product or process inside the facility. There are several methods, computer programs and models for addressing environmental impacts using LCA principles.

3.1.4. Air Emissions Control Technology

Capturing air emissions with hoods or a general ventilation system and routing them to a wet scrubber is the most common control technology for metal plating air emissions.

3.2. Benefits of effluent control and pollution prevention

To approach with pollution control is required in the industry. The selection of process technologies that achieve an intrinsically low rate of waste generation is a vital part of such an approach. Additional treatment technology to reduce the effect of the remaining residues is a subsequent step. Recycling and recovery are usually included within these two areas of consideration.

Considerable economic advantages can be expected to accompany the environmental benefit that flows from such a systematic approach to pollution control. The application of more advanced levels of technology can improve process control so as to achieve:

- Saving raw material
- Decrease in rinse water consumption.
- Decrease in the consumption of reagents for effluent treatment.
- Decrease in the size of effluent treatment facilities.
- Implementation a part of EMS and QMS
- Reduce effectively impacts to environment

Many improvements will require an initial investment such as new equipment (cost, setting up time, extra floor space), retraining of staff, possible higher energy consumption and extra supervision. Nevertheless the environmental benefits can be substantial, and even from a pure economic point of view, the resulting improvements in throughput and product quality are often enough to justify investments in cleaner processes.

3.3. Applying situation of effluent control in the electroplating industry in Vietnam

Electroplating plants in Vietnam have been not applying many solutions to effluent control and recovery, recycle wastages after plating processes. Almost the effluent control processes and pollution prevention are still spontaneous. Recover and recycling have not been implemented, the owner companies may justify due to high initial cost, infrastructure is not sensible for installing equipments, etc.

Effluent control that is not controlled in the electroplating plants in Vietnam can be shown such as:

Over consumption of water:

Rinse water contributes to over 90% of the total liquid waste generation of a typical electroplating factory in Vietnam. The need to control water usage is usually overlooked, resulting in an excessive use of rinse water which is more than the actual amount required.

Some plants are using excessive rinse water even they turn the tap on continuously without controller, even labours are also not awareness to save and limit rinse water. Afterwards, this wastewater can be direct discharged into common drainage of the plants. These can lead to an excessive use of water and the high volume of wastewater generated.

This unconscious release of rinsewater that is not realized sufficiently the limited levels can commonly cause environmental pollution in the electroplating companies in Vietnam.

Lack of control on conservation of materials

Inability to conserve chemicals is common in Vietnam, leading to an excessive loss of chemicals through wastage. Mainly mistakes include excessive dragout, improper chemical usage, poor housekeeping, poor process layout...

A number of ancillary operations may also give rise to loss of chemicals to the environment. These include:

- Storage of chemicals.
- Transfer and handling of chemicals
- Waste water treatment and discharge.
- Discharges form process control laboratories.
- Disposal of residues,
- Re-use or disposal of empty chemical containers.

Apart from that, electroplating companies in Vietnam have still lacked of training. Many improving will require an initial investment, such as new equipment (cost, setting up time, extra space), retraining of staff, possible higher energy consumption and extra supervision. These are main obstacles for companies when employ effluent controls and prevent pollution.

Every plating shop need to evaluate its own situation, so as to be able to select the best package of measures. This evaluation should include: consumption of process chemicals, water and energy, assessment of the production methods in use from the standpoint of environmental impact and the need and options for waste treatment and disposal.

Implementing on effluent control in the electroplating companies in Vietnam is necessary to have a long-time and sensible changing of production lines, infrastructure and pollution controls. Properly solutions suggestion and suitable with Vietnam conditions will be given in chapter 5

Chapter 4

Assessment and analyzing technologies of analysis methods for heavy metal

In this chapter, the author will assesses some methods for determination heavy metal that it is considered typical methods and used widely nowadays. Other methods, can applied more difficult for operating, high capital costs and high operator skill requirements, complicated or not actual suit for analyzing heavy metals in the electroplating industry (polarography, gravimetric, ion chromatography, etc). Ion sensitive electrodes and the ancillary equipment are medium capital cost but need very high operator skill to make the necessary electrodes in-house as many are not commercially available, therefore the author do not mention in this report.

Methods that mentioned including:

- Spectrometry (colorimetric)
- Atomic absorption: Flame and furnace AA
- Inductively Coupled Plasma Atomic Emission Spectrometry
- Inductively Coupled Plasma Mass Spectrometry.

Selecting the most appropriate tool for the electroplating job can sometimes appear to be a daunting task, especially since there is considerable overlap of capabilities. In fact, all of the techniques may be able to perform particular analysis at acceptable levels of accuracy and precision.

However, by evaluating the relative strengths and weaknesses of each of the techniques, particularly as their application to the practical and performance requirements of the analysis, it is possible to establish a rational basis for decision making. In other words, it needn't be all that difficult.

In this chapter will get well on way to selecting the best technique to meet lab's needs in analytical laboratories or the companies' lab.

Understanding how each technique works

This was given details in chapter 2. While it isn't necessary to grasp the entire complex technological details of each of the various elemental analysis instruments, for comparison purposes it is helpful to have a general understanding of basic principles.

Real-world questions to ask when appreciation of different instruments:

- What is the application?
- What are the sample types to be analyzed?

- What elements and concentration ranges are required?
- How many elements will be determined per sample?
- What are the accuracy and precision requirements?
- How many samples will be analyzed per day?
- Who will be operating the instrument?
- What level of operator expertise is available?
- How much lab space is available?
- And finally what will the budget allow?

4.1. Application

Actually, all of the various techniques are used in broadly similar application areas, such as Environmental, Metallurgy and Mining, Pharmaceutical/Biotech, Semiconductor Manufacturing, Agriculture, Food & Beverage, Chemicals/Petrochemicals, Clinical and Utilities. Application is necessary for operators; therefore they can decide which instrument is most suitable for their purpose. In this part, the author will only mention to apply for environmental field, especially can be applied for electroplating industry.

Spectrophotometry (Colorimetric)

Wide application range from main and minor component analysis to trace analysis of numerous transition metals, e.g. Fe, Co, Ni, Ti, Cu, Pb, Zn...

Though colorimetric is mainly used for determination of metal ions, it can also be used for analysis of some organic metal additives such as saccharin or coumarin.

Flame atomic absorption spectrometry

FAAS can be applied to a wide range of elements, provided a suitable light source is available. In choosing among AAS techniques, FAAS should be considered first or second if simultaneous ICP-AES is available, in the determination of Li, Na, Mg, Al, K, Ca, Mn, Fe, Ni, Cu, Zn, Cd, Ba, and Pb. FAAS has been widely used with adapter for flame gases and atom traps for the measurement of toxic metals such as Cd, Pb, with respective detection limits of 0.1 and 1 µg/l

Graphite furnace AAS

The graphite furnace is applied to a wide variety of samples, can be equipped with an autosampler for unattended operation that utilizes the Zeeman effect for background correction is also available for some instruments.

This method is very suitable for determination of metals in groundwater, surface water, drinking water, storm runoff, industrial and domestic wastewater, sludge and soil.

The graphite furnace, which requires only few microliters of sample, is ideal for ultra-trace determination of more than 60 elements. It can provide detection limits 1000 times lower than those of conventional flame techniques.

ICP-AES (OES)

Environmental applications utilizing ICP-AES (OES) for metal determination encompass a wide range of materials, such as natural waters, solids, sediments, biological tissues and air particulate.

ICP-AES (OES) can measure metals or some nonmetals. This method is applied to the following analytes: Li, Be, B, Na, Mg, Al, P, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Sr, Mo, Ag, Cd, Sn, Sb, Ba, Ce, Hg, Ti, and Pb.

Simultaneous determination of main, minor and trace elements, inductively coupled plasma-atomic emission spectrometer: an instrument capable of determining the concentrations of 40 to 70 elements simultaneously by measuring the intensity of light given off by samples. In the other hand, ICP-AES can determine nonmetals as Cl, Br, I.

ICP-MS

The application of ICP-MS are broadly similar to those for ICP-AES, although the better sensitivity of the former has resulted in applications such as the determination of ultralow levels of trace elements. ICP-MS technique has been employed to determine a large number of elements in environmental sample and it especially suited for heavy metals analysis in groundwater samples, surface waters and drinking water using a quadrupole mass analyzer in scanning mode. It may also be used for determination of total recoverable element concentrations in these waters as well as wastewaters, sludge, and soil samples. This methods is applicable to the following elements: Be, Al, V, Cr, Mn, Co, Ni, Cu, Pb, Zn, As, se, Mo, Ag, Cd, Sb, Ba, Ti, Th, and U. the major drawback of ICP-MS is its expense and that is gradually reducing.

4.2. Detection limits

The detection limits can be achieved by the various techniques may help we decide which tool is best for the task.

ICP-MS produces the best detection limits (typical 1-10ppb), followed by GFAAS (usually in the sub-ppb range), then ICP-AES (of the order of 1-10ppb), FAAS (in the sub-ppm range) and the last is spectrophotometry method (ppm).

The Figure 4.1 below shows typical detection limit ranges for each of the techniques, including variations such as both radial and axial ICP.

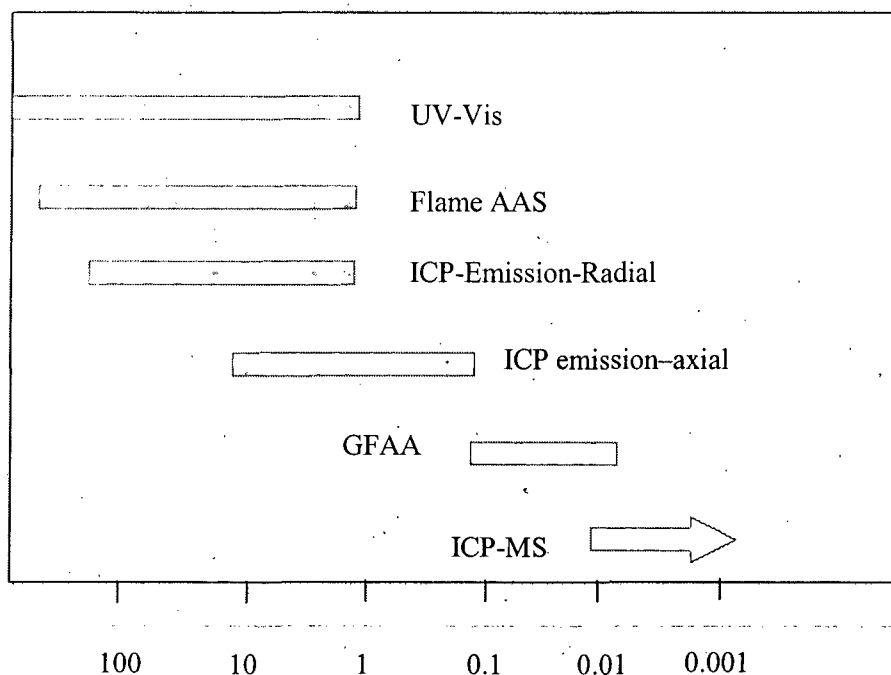
Typical detection limit ranges for the major Spectroscopy techniques

Figure 4.1 Detection limit ranges, µg/l

4.3. Precision

“Precision” is a measure of the confidence you can have in your measured results. The lower the % RSD (Relative Standard Deviation) of the results, the higher is the confidence.

Precision is more important to choice which methods are suit for analytical purpose. There are 2 types to assess precision:

- Short-term precision generally refers to measurements made over a period of 5-10 minutes;
- Long-term precision is generally measured over several hours of operation.

UV/VIS: About 0.5 - 2 %

FAAS

Short-term precision is in the range of 0.1-1.0%. The long-term precision depends on the spectrometer optics; double beam types are capable of long-term precision of 1-2%, where single-beam optics are typically in the 5% range.

GFAAS

Primarily, short-term precision is generally in the range of 0.5-5% because of difficulties in injecting very small volumes. Long-term precision is highly dependent on the tube type and condition.

ICP-AES

Short-term precision is reasonably good, around 0.1-2%, and even over periods of several hours, should be no worse than 1-5%. Simultaneous spectrometers (where all the analyte measurements for a sample are made at the same time) generally have superior short- and long-term precision compared to sequential systems (where measurements for each analyte are made one after the other). Use of internal standardization can significantly improve precision for simultaneous instruments.

ICP-MS

Short-term is in the range 0.5-2%, with long-term precision around the 4% level. Use of internal standardization or the more costly method of isotope dilution can significantly improve precision.

Long-term precision in any of the techniques can be improved by more frequent instrument calibration or drift correction techniques.

Generally samples with higher matrix levels will exhibit worse short and long-term precision. The use of internal standards and drift correction in ICP and ICP-MS will dramatically improve results.

4.4. Dynamic Range

Dynamic range of the various techniques is important, because it directly affects the amount of dilution necessary in preparing solutions. A wider linear range means fewer standards are needed.

- *UV/VIS* have range in $10^2 - 10^3$
- *FAAS and GFAAS* have limited dynamic ranges, of the order of only $10^2 - 10^3$; therefore solutions must be held in a narrow range of concentrations.
- *ICP-AES* has a considerably wider dynamic range, up to 10^6 , making it a more suitable technique for highly concentrated samples, or samples with widely varying concentrations of analyse elements. It can be considered a technique capable of measuring from trace to percent levels.
- *ICP-MS* typically operates at much lower concentration levels so that linear ranges up to 10^8 can be achieved for some analyses. In standard practice, however, ICP-MS is a technique for ultra-trace to trace levels to ppm levels.

4.5. Elemental Interferences and Other Problems.

All of these elemental analysis techniques suffer from various interference effects. The severity of these effects can make a big difference in results for real samples. Broadly

speaking, interferences can be classed as: *Spectral*-due to atomic or molecular fine structure in the spectrum; *Background* – due to broad features or electronic baseline; *Matrix effects* – primarily due to physical or chemical influences.

Spectrophotometry

- *Spectral*: particulate matter, nitrate/nitrite, chlorine, and/or ozone in the sample. The nitrate used to lower the pH of our samples may have interfered with the absorption spectra by giving a higher absorbance than for sample alone.
- *Background*: from nonabsorbing organic material present in the sample: Simple sugars, aliphatic acids, alcohols and amino acids; such as glycine, do not absorb in the UV range. However, these compounds are those most likely to be consumed by microbes as food, and are not expected to be present in natural water samples electroplating industry at high concentrations.

Particulate matter can affect the UV-Vis absorbance by scattering incoming radiation.

Flame AAS

- *Spectral*: There are virtually no spectral interferences of any significance in flame AAS.
- *Background*: Background effects do exist and have to be compensated for by using some form of background correction. A deuterium-based lamp is commonly used for this purpose.
- *Matrix effects*: These are more serious, although use of the hotter N₂O/acetylene flame can minimize many of the chemical effects. Ionization becomes a problem when the hotter flames are used; ionization buffers are required. Viscosity/surface tension effects in the spray chamber/nebulizer can require the use of matched standards.

Graphite furnace AAS

- *Spectral*: There are virtually no spectral interferences in graphite furnace AAS.
- *Background*: Background effects do exist on a major scale and have to be compensated for by using deuterium or Zeeman background correction. The background usually arises from vaporized matrix components which are being atomized at the same time as the analyte.
- *Matrix effects*: These can be very serious and generally occur in the vapor phase; various chemical modifiers and platforms within the graphite tube are used to control these interferences. In addition, injection of samples into the tube is subject to viscosity/surface tension problems.

ICP-AES

- *Spectral:* Spectral interference problems are fairly common in this technique due to the line-rich spectra produced by the hot plasma source. They can be minimized by using high-resolution spectrometers or using inter-element correction factors. The simplest cure is to move to an alternative analyte line (although this may cause a loss of sensitivity).
- *Background:* Background effects do exist in ICP-AES and require the use of off-line background correction techniques, or, increasingly, sophisticated chemometrics. Molecular species (such as OH from the water solvent) can cause peak or band structures. It may be possible to minimize them by careful selection of plasma conditions or moving to an unaffected analyte line.
- *Matrix effects:* Chemical matrix effects are minimal, but physical effects such as viscosity and surface tension effects in the spray chamber/nebulizer mean that matched standards may be required. Use of an internal standard is a common way of overcoming this problem.

ICP-MS

- *Spectral:* Spectral interference problems in ICP-MS are relatively few and well-documented. They occur when species (which may be molecules or doubly-charged ions) have the same or very similar mass as the analyte. They are known as isobaric interferences and cannot be resolved at resolutions typically found in common quadrupole mass spectrometers. Inter-element correction factors can be used (similar in principle to inter-element correction factors in ICP-AES) or other, lower abundance isotopes must be selected with a resulting loss of sensitivity. Many of the interferences can now be overcome using cool plasma or collision cell technology to break up the molecules or by using high-resolution magnetic sector ICP-MS.
- *Background:* No broad background species exist for MS as can be found with optical techniques. Electronic background is low, but is a factor that can differentiate some ICP-MS systems. Many ICP-MS determinations are said to be "background limited," which is a term that signifies that the contamination in the blank or memory effects which limit the detection limit. At the part-per-trillion level, this can be significant.
- *Matrix effects:* Chemical matrix effects can be a problem in ICP-MS, resulting in impaired accuracy if not addressed. They result from the presence of the argon plasma gas and also the solvents/acids used in preparing the samples. For this reason care should be taken when choosing the acids for dilution, nitric acid being the preferred choice.

In addition, physical effects (such as viscosity and surface tension effects in the spray chamber/nebulizer) may require the use of matched standards. As with ICP-AES, use of an internal standard can overcome this problem.

4.6 Ease of Use

- *UV/Vis*: the most easy to use.
- *FAAS* systems are usually very easy to set up and run. They are capable of some degree of automation but should not be run unattended, due to the flammable gas risk. Method development is easy and a vast library of methods exists.
- *GFAAS* systems are somewhat more difficult to set up because of the accuracy of sample injection required to achieve the best results. Also, the limited working lifetime of the graphite tubes requires more frequent set up. Furnace method development can be difficult, and may require considerable expertise. Fortunately, a substantial methods library exists. Furnace AA systems are capable of a high degree of automation; because they only use inert argon gas, they can safely run unattended.
- *ICP-AES* systems are easy to set up and have to be adjusted relatively infrequently. If there are major spectral interferences, method development can be complicated; however, the use of high-resolution spectrometers can minimize this problem. In general, though, method development is moderately easy, although the library of methods is less than for the AAS and GFAAS techniques. ICP are capable of a high degree of automation, and can run unattended.
- *ICP-MS* systems are getting easier to set up for routine analysis. Some parts of the system (e.g., the interface cones) may need regular attention to preserve performance. Method development can be more involved than with the other techniques and requires a higher level of expertise. ICP-MS systems can be fully automated, and can run unattended.

4.7. Operator Skill

Not every technique requires a trained scientist for everyday operation. In fact, there is an increasing trend in many industries to use less skilled technicians for routine analysis tasks. Although today's software has greatly simplified the operation of even the most complicated equipment, software can't substitute for understanding. It is important to consider the technical level of laboratory personnel who are going to be operating the instrument, and to allow for additional training or possibly even additional staff if required.

Generally, flame AAS and colorimetric is quite easy to set up and to use, and requires minimal operator skill. Furnace AA can be considerably more difficult to operate, calling for a relatively high level of knowledge and ability. ICP-AES falls between these two, particularly for production-type applications, and is a bit easier to master than GFAAS, both in view of modern software capabilities, and the considerable body of literature available.

ICP-MS is a newer technique. Its application library, while growing rapidly, is not as complete as for the other methods. To consistently achieve superior results and reliable, high-quality data, you will probably need a somewhat more skilled person in charge of the instrument, although setting up the machine to run redesigned methods is a simple process.

4.8. Speed of Measurement

How many samples can a particular technique analyze in a given time? How many elements can be determined? For each sample, the measurement cycle consists of three steps:

- *An equilibration period* in which sample is taken from the sample container, transported to the sample cell, and the analytical signal reaches stability. ICP-MS and ICP-AES systems have similar new sample delay times, which may be up to 60 seconds long. FAAS is much quicker, typically only about 5 seconds. GFAAS systems can take up to 2 minutes to dry and ash the sample prior to measurement. Colorimetric method can measure 10 seconds per sample.
- *A measurement period* during which the signal is measured for the element and, if necessary, their background points.
- *A rinse-out period* during which the sample is removed from the source. This step may be carried out concurrently with the first; i.e. the next sample may be used to rinse out the previous one.

For AAS and sequential ICP-AES systems, there is a further period while the next element line is selected.

ICP-MS and simultaneous ICP-AES systems make the fastest measurements; all analyses in a sample can be measured in about 2-5 minutes. Sequential ICP-AES systems take about 10 seconds per analyse line, including the time taken to select the line. The sequence is to measure all the analyses in a sample, one after another, then go to the next sample and measure all the lines again.

UV/VIS generally requires about 4-10 seconds per measurement, but sequence of operation is different.

All samples are measured at a single analyse line, then the next lamp is selected and all samples are measured again. GFAAS measurement time is less than 5 seconds for a single result at a single analyse line. However, several repeats per sample may be necessary with GFAAS to obtain satisfactory precision.

Overall the speeds are typically as follows:

ICP-MS:	All elements in 2-5 minutes
ICP-AES (Simultaneous):	All elements in 2-5 minutes
ICP-AES (Sequential):	5-6 elements per minute
FAAS:	4 seconds per element
GFAAS:	2-3 minutes per element
UV/VIS	10-20 seconds per element

The total analysis time taken by the different techniques will depend on the number of elements to be measured per sample. As a result, the speed parameter provides a relatively solid base for deciding on one technique over another (all other factors being equal):

- For less than 5 elements per sample, FAAS is often the quickest technique, depending on the total number of samples.
- For 5-15 elements, sequential ICP-AES is the optimum choice.
- Above 15 elements, either ICP-MS or simultaneous ICP-AES is the best choice.
- GFAAS will always be the slowest of the techniques (however, it may still be the method of choice for other reasons).
- For 1-2 elements, colorimetric is best choice technique.

4.9 Cost

Finally, there's the budget not just the initial cost of the capital equipment, but the true cost of ownership, which includes getting the lab ready for the instrument, and the actual cost of running samples. The purchase cost is very straightforward and usually well-understood, but the other two are often forgotten or underestimated.

Capital costs

Obviously, because there are many instruments available from a number of manufacturers, and because so many options and configurations are possible, it is difficult to put absolute values on capital costs. However,

the table below can serve as a starting point. Depending on accessories or options may add considerably to the purchase price. Roughly, can expect to pay from around \$15-20,000 for a base configuration flame AA system, and compute the other costs from there.

Table 4.1 Relative System Costs

Colorimetric	1 x
Flame AAS	7 x
Furnace AAS	14 x
Sequential ICP-AES	30-35 x
Simultaneous ICP-AES	35 - 50 x
ICP-MS	70 - 140 x

Installation costs

A laboratory may require significant changes before adding an elemental analysis instrument.

For example:

- All these systems require fume extraction.
- ICP-MS or GFAAS sometimes require clean room conditions to operate at the ppt level.

- ICP-based systems (ICP-AES or ICP-MS) require high volume gas installations.

For GFAAS or ICP-MS use, reagents may also need to be upgraded from normal analytical grade to high-purity grade. AA-grade standards, which often contain minor impurities, are suitable for UV/Vis and AA analyses, but are not adequate for ICP-AES or ICP-MS.

Finding considerable variations in the quantities of common supplies like argon, for instance, consumed during an analysis. GFAAS only uses about 3.0 L/min of argon; ICP-AES and ICP-MS both require around 15-20 L/min.

Operating costs

The following table outlines the typical consumable items and utilities required by the various techniques.

Table 4.2 Some accessories combined with different methods

UV/Vis	Reagents and standard power, curvet
Flame AAS	Acetylene/nitrous oxide gases (compressed air source) Hollow cathode lamp reagents and standards power
GFAAS	argon gas, hollow cathode lamps graphite tubes and cones reagents and standards, power, cooling water
ICP-AES	argon gas, quartz torches, reagents and standards pump tubing, power, cooling water
ICP-MS	argon gas, quartz torches, sampling and skimmer cones reagents and standards, pump tubing, power, cooling water

Calculation of detail costs for operating is very different for each equipment. Analysis by ICP-MS and ICP-AES has to spend a lot argon gas (about 15 liters/minute). Time for standby equipment also take so long. These methods only suit for measure many samples at the same time.

See this table, a relative consideration can determine that ICP-MS has operating cost is much expensive than ICP-AES then to GFAAS, FAAS and finally to UV/VIS. However, in case analysis a lot of elements in the same time, ICP-MS and ICP-AES best implementation.

4.10. which instrument is most suitable?

Therefore, it is unlikely that a single technique is going to perfectly suit all of a laboratory's needs. Based on what things we have: space, skilled staff, and a surplus budget, we will probably have to make some compromises.

The following table summarizes the discussion above parts, all features and strength and limitations of each of methods. Afterwards, which method is most suitable for our purpose is will be determined.

Table 4.3 Summary of elemental analysis techniques

	UV/Vis	Flame AAS	GFAAS	ICP-AES	ICP-MS
Detection limits	Good for some elements	Very good for some elements	Excellent for some elements	Very good for most elements	Excellent for most elements
Sample throughput	30-60 seconds per element	10-15 secs per element	3-4 minutes per element	1-60 elements/minute	All elements in < 1 minute
Dynamic range	10^3	10^3	10^2	10^6	10^8
Precision	0.5-2%	0.1-1%	0.5-5%	0.1-2%	0.5-2%
Short term		2-beam 1-2%	1-10%	1-5%	2-4%
Long term		1-beam < 10%	(tube lifetime)		
Interferences					
Spectral	Very few	Very few	Very few	Many	Few
Chemical (matrix)	Many	Many	Very many	Very few	Some
Physical (matrix)	some	some	Very few	Very few	Some
Dissolved solids in solution	5%	0.5-5%	> 20% (slurries)	0-20%	0.1-0.4%
Elements applicable to	43	68+	50+	73	82
Sample volume required	Large	Large	Very small	Medium	Very small to medium
Semiquantitative analysis	No	No	No	Yes	Yes
Isotopic analysis	No	No	No	No	Yes
Easy to use	Very easy	Easy	Moderately easy	Easy	Moderately easy
Method to develop	Very easy	Easy	Difficult	Moderately easy	Difficult
Unattended operation	No	No	Yes	Yes	Yes
Capital costs	Least Low	Low	Medium to high	High	Very high
Running costs	Very Low	Low	Medium	High	High
Cost per element analysis					
High volume-few elements	Very low	Low	High	Medium	Medium
High volume-many elements	low	Medium	High	Low-medium	Low-medium

Summary about typical detection limits of elemental analysis techniques

The following detection limits are calculated at 3σ (3 sigma detection limits in deionised water). The detection limits listed are representative of the technique and do not represent the performance of a particular instrument. All ICP-MS values are based upon quadrupole ICP-MS performance; lower levels of detection are available in magnetic sector ICP-MS systems.

Table 4.4 Typical detection limit ranges for the major Spectroscopy techniques Precision

Element	UV-Vis (ppm)	FAAS (ppb)	GFAAS (ppb)	ICP-AES (radial) (ppb)	ICP-AES (axial) (ppb)	ICP-MS (quad) (ppt)
Ag	0.02-2	2	0.05	2	0.5	0.01-0.1
Al	0.02-0.7	30	0.25	6	1.5	0.1-10
As	0.002-0.1	300	0.33	12	2	1-10
Au	-	8	0.15	6	0.6	0.01-0.1
B	0.01-1	500	43	0.5	0.2	10-100
Ba	-	20	0.4	0.2	0.04	0.01-0.1
Be	-	1	0.025	0.2	0.06	0.1-1
Ca	-	1	0.04	0.03	0.03	1-100
Cd	0.002-20	1.5	0.02	1	0.1	0.01-0.1
Co	-	5	0.5	2	0.5	0.1-1
Cr	0.005-10	6	0.025	2	0.4	0.1-1
Cu	0.001-0.3	3	0.07	2	0.3	0.1-1
Fe	0.01-4	6	0.06	1	0.3	0.1-100
Hg	-	145	18	9	1.2	1-10
K	-	2	0.02	6.5	0.5	0.1-100
Mg	-	0.3	0.01	0.1	0.03	0.1-1
Mn	0.01-5	2	0.03	0.3	0.05	0.1-1
Na		0.3	0.05	1	0.2	0.1-100
Ni	0.02-10	10	0.24	6	0.4	0.1-10
Pb	0.002-20	10	0.04	14	1	0.01-0.1
Se	0.001-0.25	500	0.65	20	5	1-1000
Si	-	200	0.8	5	2	> 1000
Sn	-	96	0.6	0.1	0.01	0.01-0.1
U	0.001-0.01	40000		3.5	0.4	0.01-0.1
V	0.05-40	50	0.7	2	0.5	0.01-10
Zn	0.004-20	1.0	0.0075	1	0.06	0.1-10

Table 4.5. Comparison of the analytical methods used for determining heavy metals

Analytical methods	UV/VIS	FAAS	GFAAS	ICP-AES	ICP-MS
Advantages					
Inexpensive	x	x			
Multi-element analysis				x	x
Isotopic analysis					x
Large linear working range				x	x
Low concentrations			x		x
high sample throughput				x	
DISADVANTAGES					
Sample dissolution	x	x	x	x	x
Expensive				x	x
Single element analysis	x	x	x		
Elemental interferences	x			x	
Limited working range			x		
Low sample throughput			x		

Base on all assessment and comparison above, the author can suggest which methods are most suitable for electroplating companies and for monitoring central. Addition to, they can know clearly each technique and can choose for themselves whatever techniques they want provided that can meet sufficient they demands.

4.11. Benefits of modern analytical methods can apply for electroplating industry

Although the modern analytical methods have to a lot of money for investment and operating but benefits it can receive extremely, their features and strengths have been recognized in over the world.

AAS	ICP-AES	ICP-MS
<ul style="list-style-type: none"> - Most valuable technique for electroplating heavy metals analysis. - Very simple to use, reliable and cost effective. - Detection limits is most suitable for analysis heavy metals in water of electroplating industry. - Fast determination 	<ul style="list-style-type: none"> - Simultaneous or sequentially measure the concentration of 20 elements is equivalent than AAS - Fast determination for lot elements at the same time. - Can simultaneous analysis - Very suitable for analysing when have a lot samples. 	<ul style="list-style-type: none"> - Powerful tool for trace and ultra-trace elemental analysis - Rapid multielement determination - Fast speed - Isotopic capabilities - High resolution

Chapter 5

Suggestion of analysis methods

For chemical substances and effluent control in Vietnam

5.1. Benefits when implementing of analytical methods in electroplating industry

Analytical method considered as a tool to monitor and control performance in the plating industry. Although many plating solutions allow for optimum performance over a wide variation in solution composition, the information becomes more critical during malfunction.

Why have to measure and analytical control?

All perform optimally only when their chemical composition lies within set limits. Too concentrated, too dilute, incorrect pH, too high a concentration of impurities - these are just some of the parameters which must be maintained at the correct level, if the performance of a plating plant is to be optimised.

The composition of process baths, including pretreatment and post-treatment baths, should fall within a compositional range, often specified by the process or bath Supplier. Consequences can occur commonly if concentration of chemical substances in plating baths incorrect or it contains impurities:

1. Bath too concentrated

If the bath contains excessive concentrations of acids, alkalis, buffers, the main reagents (metal ions, cations), organic or inorganic additives, the consequences could be:

- Defective work and too many rejects can make increase production costs, needless chemicals costs.
- The greater the concentration, the greater the rate at which organic compounds will break down, in solution or at the anode or cathode. Also the greater the bath concentrations, the more chemicals will be contained in the dragged-out solution, and so lost.
- Needless additional load on the effluent treatment plant, include chemicals used to treat these effluents, and in some cases, payments to the Water Authority.

2. Bath too dilute

If the bath is too dilute in some or all of reagents, the possible consequences could include:

- Defective work
- If the electrical conductivity is too low, cell voltage will be needlessly high. Electrical energy wasted, and maybe problems with excessive bath heating.

3. Bath contains impurities

Impurities can build up in process baths in many different ways, for example by being carried in by the work, or liquids adhering to the workpiece.

The presence of impurities, anions, metallic cations, inorganic or organic species above a certain concentration, will certainly result in defective workpiece. Reworking such defective components is expensive and companies can lose good customer and a good reputation in the industry. It takes years to rebuild a bad reputation.

Higher than optimum concentrations also represent a high operation cost to companies. Therefore regular bath analysis is one of the best investments a necessary operator makes.

Many benefits can get from analytical employment as:

Firstly, it prevents wasteful and needless use of chemicals, in the main those which require to be regularly added as replenishments. Quite apart from the fact that too high a concentration is detrimental to the finish, significant savings can be made by avoiding their needless addition.

The second benefit associated with avoiding needlessly high concentrations of species drag-out effects. The amount of species in solution and into the subsequent process solution is linearly proportional to concentration of that species in solution. Needlessly high reagent concentrations will result in higher rinsing water use, increased effluent treatment operations.

Analytical methods are the foundation of plating-bath control. By the use of analytical control it is possible to hold a bath limits. By frequent analyses and continuous adjustment of chemicals, baths have been operated for years without trouble.

For most establishments, a proper process control will do much to help the owner/manager in the efficient operation of plants' body. A laboratory will help in:

- Reduced need for treatment, and less sludge for disposal.
- Trouble shooting to reduce rejects caused by out of control situations.
- Efficient operation of treatment baths, determination of dumping frequencies by test rather than habit, control of addition to processing baths.
- Longer maintenance and Extent bath' life
- Capability competitive enhance on exporting of product
- In case having breakdown for plating bath, companies can analyse of chemical substances quickly without waiting for a long time if they sent sample to the analytical service or other organization.

Furthermore, when analyzing chemical substances in plating bath and in wastewater nearly all electroplating companies will meet requirement of regulations and environmental law. Companies will comply with EMS and QA efficiently and meet a part of quality assurance system and solve customer' problems.

5.2. Suggestions

Product quality is one of the prime factors in ensuring consistent marketing of electroplating industry. It is well known that quality is a combination of various parameters demanded by consumers such as appearance, shape, size, colour etc.

The quality operating system developed by plating companies should be established to be compliant with ISO 9001, QS 9000.

Relatively basically task of implementing QA in a company as follows:

- Policies and objectives determination of QA compliance with ISO 9000 families.
- Management review and internal audit
- Design control
- Documentation and change control
- Process control
- Receiving inspection
- Inspection and testing
- Production and measuring equipment
- Indication of inspection status
- Handling, storage, packaging, preservation and delivery
- Training
- Servicing

The ISO-9000 system is particularly effective in keeping the preventive action and root cause/corrective-action systems robust and effective. A series of internal system audits, product audits, and external audits takes place regularly to monitor the effectiveness of the system and are conducted by in-house personnel.

Steps implementation of QA can recognize that monitoring and checking solution plating baths, products are very important in QA due to directly affect to product' quality. Quality control; or more broadly quality assurance, is an essential part of the conduct of an analytical laboratory. A full treatment of the many management, planning, record keeping, and audit procedures is beyond the scope of this article.

Procedure control of a plating process includes: control on surface treatment, control on plating bath and control on post treatment to final product. This part, the author will concentrate on quality control throughout analysis of chemical substances in plating bath.

At present time, due to causes about the implementation costs, enterprises' awareness and this problem still new for plating companies in Vietnam, quality assurance system might have a long time to adopt. The first skill and necessary for implementation QA for plating companies are procedures monitoring, analyzing and effluent control. This implementation means that electroplating companies Vietnam will implement an essential part of quality assurance system and plating companies can know clearly why they should implement QS.

5.2.1 Suggestion for analytical methods in plating baths

Analytical methods that suggested for the electroplating companies in Vietnam based on some main factors as follows:

- Reference of analytical methods that countries in the world have been applied.
- Comparison and assessment about benefits and features of each method
- Originate from fact conditions of electroplating companies in Vietnam

Other important characteristic is from the past to now the supply houses play a pivotal role in the continuing viability of the industry, particularly for the very small companies. Not only do they supply chemical solution for plating and reagents/methods for analysis, they also offer analytical services to their clients. They maintain laboratory facilities containing a wide range of sophisticated instrumentation and the trained staff to solve their customer problems. It is perhaps inevitable that the service provided by the supply houses will become more expensive to the client, and more closely linked to the volume of trade with the supply house. This has been increasing of product price and sometime the analytical time depends on supplier.

Like this, the smaller companies may have to enter into a separate service contract for analytical services of they have to be employed independence analysis by themselves.

There is a variety of analytical equipment for monitoring the analytical concentration of plating additives as description in chapter 2. In fact, polarography and ion chromatography are not considered to be good analysis for development as routine methods in the plating industry due to their relatively high capital costs and high operator skill requirements. Ion sensitive electrodes and the ancillary equipment are medium capital cost but need very high operator skill to make the necessary electrodes in-house as many are not commercially available

With characteristics is small scale, old technology, application of modern methods cannot implement by electroplating companies in Vietnam. In my opinion, in this time volumetric methods is considered the most suitable for plating companies in Vietnam to analyse of chemical substances in plating solution effectively.

Volumetric methods now are still using widely and analysis of solutions by titration, often referred to as volumetric analysis, is one of the oldest methods and the simplest in analytical chemistry. In spite of this, it remains a rapid and convenient, as well as a most accurate procedure. Cost for equipment is less expensive than for other methods. In the other hand there are literally dozens of textbook on analytical chemistry where the theory and practice of titration is treated.

Titrimetric method is very easy to use, relatively fast simultaneous can determine anions and cations in plating solution.

Preliminary calculation of costs for analyzing chemical substances by titrimetric method is given in table 5.1 (for a company are plating about 3 metals or more and have 3 titration equipment)

Table 5.1 Relative Costs
When implementing titrimetric method per year can be calculated

Content	Cost (USD)
Investment cost for equipment and accessories	3 x 300 = 900
Chemicals	700
Other cost	Insignificant
Total	1600

These costs are not much for small companies, but in fact, the awareness for implementing and the skill of operator whether meet or not. Therefore, companies should have plan appoint the operator to educate at the university or research plants.

Colorimetric tests also should be performed by larger companies due to its simplicity, ruggedness, ease to use and low cost. This method can determine accuracy anions and cations in plating bath and effluents. It can be adapted fairly easily to carry out a range of analytical measurement. Companies should be applied this method due to it can analyse widely anions and cations in plating bath and in effluent.

Good implementation of these methods frequently in house-lab not only helps companies save chemical, raw materials, assure quality product considerably but also improve competitive in market. They have basis to report with environmental protection offices as well and can submit customers when they have requirement.

For smaller companies (about 5-10 people), implementation in analysis of plating bath can cause difficulties about cost and the employed operator also precarious.

Companies should create small groups of people who work together as they study, either working independently or in a small group is equally successful. It appeared that there was considerable concern within the industry, with respect to both the methods of chemical analysis currently in use to monitor the levels of active constituents in plating baths and the skills of the staff undertaking these measurements. The smaller companies also rely on classical analytical techniques, frequently carried out by staff with little if any formal analytical training.

Titrimetric and colorimetric methods should be employed at the present time for the companies. However, if companies want to improve the best products, method is more modern and better can orient for future.

Whereas larger companies could approach the investment in some of the newer analytical measurement technologies (e.g. those based upon atomic spectroscopy and X-ray fluorescence) operated by a skilled workforce,

Definitively, with plating solutions have complex constituent and product requires higher quality if implemented by the companies' technician possibly resulting in the product quality is not desire. Therefore some of the more difficult analyses should be carried out by external testing laboratories or as a service provided by the chemical suppliers.

5.2.2 Process control by analysis of chemical substances in plating bath in Vietnam electroplating companies

The environment has a significant effect on product quality and reliability. Therefore, control items, control methods and control standards for temperature, contamination, concentration of chemical substances in plating bath, dust and other items are set according to the manufacturing process and the environment is maintained and controlled by monitoring system. In addition, quality is also maintained and controlled by monitoring the specific resistance, purity and other characteristics of the deionised, equipment and chemicals used in manufacturing lines.

In order to offer on a timely basis products that answer the needs of customer, electroplating companies should establish and uses quality systems adapted to the demands of customers throughout the world that use international standards for quality assurance such as ISO9000 that cover the entire process from the product planning stage to development, design, trial production, evaluation, mass production, shipping and servicing.

Electroplating companies in Vietnam now should approach toward quality assurance to improve product and service quality.

In the development and design stage, system design, circuit design, structure design, production method design is all conducted in parallel. Testing is particularly important in the design stage for complex and advanced product.

So that, how to performance of the analytical process control?

5.2.2.1. What is companies analysing and how long they have to do it?

First of all, companies have to decide what they are going to look for. First task will be to determine the concentrations of all known bath constituents, as set out by the Supplier. Looking for impurities - contaminating species - is more difficult because in many cases, have to take a guess at what the contaminant might be. So the best approach is to start using Qualitative Analysis. If plating or other components have an obvious defect, operator can try another approach.

No discussion of controlling plating processes would be complete without mentioning bath maintenance. At companies, the analytical chemical laboratory is the focal point of the quality control measures that are used for plating solutions. Hull cell analysis, a diagnostic check, visually monitors brightener levels in the plating bath. By analyzing plating baths daily and weekly, chemistries can be maintained to the highest standards.

It is really important to know the chemical composition of plating solutions.

5.2.2.2. Taking sample and analysis

How to Process control to achieve best result? How can take a sample from the solution in the bath, and analyze it, using usually a chemical analysis method correctly?

Some factors need to be considered as:

a. Sampling is not a cinch

Sampling, sample handling, and matrix effects

Have to consider carefully how to take a meaningful sample. The composition of a process bath may differ from top to bottom of a tank, or as between inlet and outlet. The composition may differ when the bath is working and when it is idle. There may be zones in the bath, especially if it is not thoroughly stirred, which are more or less dilute than the rest of the bath. Chemical and electrochemical reactions take place at or around the anodes and the cathodes – sampling too close to these could give the wrong answer.

Carry out some simple tests to see whether any of the effects noted above are reflected in the results given by the following analysis.

Great care is required in taking samples, sample handling, and accounting for matrix effects to avoid contamination, sample degradation, or other artifacts. Use of certified reference materials, if available, is also required.

b. Look after your sample

- After taking sample try and carry out analysis procedures as soon as possible.
- Don't let sample become heated or be exposed to direct sunlight, before analysis. In some cases don't forget that the solution can react with the container (when this is made of glass) and this will certainly result in a false result.
- Stick label on each sample. When and where it was taken, maybe who took it. Use a label which won't wash off by mistake.

c. Analyzing

So have a sample of solution, maybe 100 ml or so, and want to analyze it.

Operator considers sample and then implement according to instruction documents. Qualitative Analysis will hopefully tell us what species are present but not in what concentrations. Quantitative Analysis will give us this additional information. Analysis is somewhere in between, giving us a rough idea of how much of a given species is present.

In addition operators also should consider influences on analytical process and calculate results precisely.

Detail process control of analysis of chemical substances in plating bath is given in Figure 5.1. This process generally applied for plating procedures in the world and I should think, electroplating companies should the best implement this analytical process.

This is also efficient process control and if companies comply with correct procedure the analytical result will always exactly.

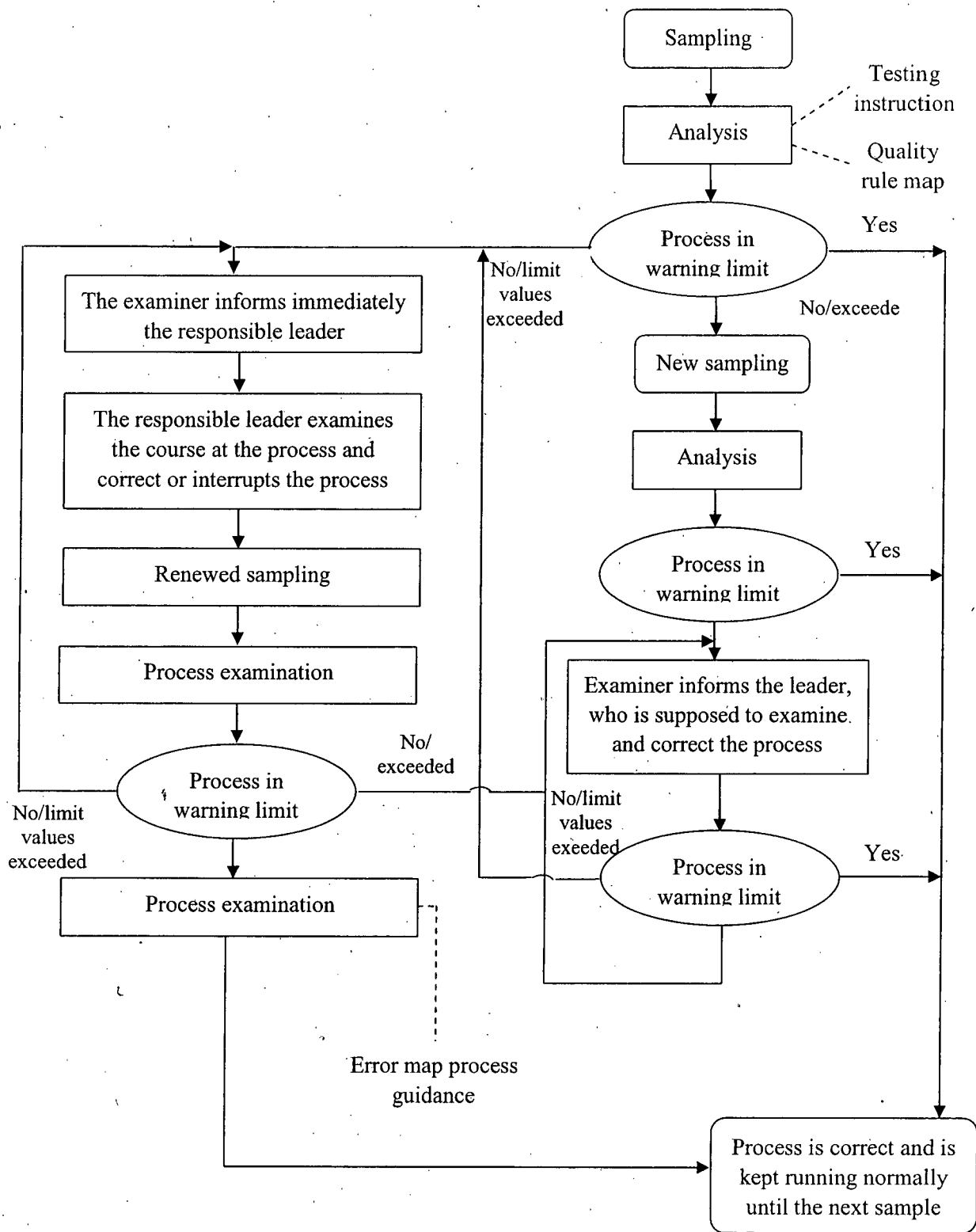


Figure 5.1 Schematic diagram of the analysis process control in plating solution

Control charts will be set up and used to record results from selected function and control checks to determine when or if the testing or analytical process is out of control and record the results of corrective action taken.

Control checks will be performed during the analytical or testing process. These checks are made on all analyses or tests, and intermittently after a specified number of procedures have been completed.

The results from selected function checks and control samples will be recorded on control charts: to track events showing that the system is out of control, to indicate what part of the system is the source of the error and to provide an indication of the results of any corrective action taken.

5.2.5.3. For controlling of measuring tools and equipment

This procedure is used to control the accuracy of measuring, test and calibration standards. Measurement standards used for the calibration of measurement tools shall be traceable to plating products and be at least four times the accuracy of the tool they are used to calibrate. Calibrations are performed on daily, weekly and annual basis as required by the type of tool and the environment they are used in. Calibration intervals are established to the extent necessary to ensure continued measurements of the required accuracy. Measurement and test equipment shall be stored and handled in a place that will not adversely effect the calibration or the condition of the equipment.

Environmental conditions: measuring and test equipment and calibration standards will be calibrated in an area that provides control of environmental conditions to the extent necessary to ensure required accuracy and precision. Employer should see the supplier' instruction document to calibrate the tools and equipments.

The calibration of laboratory instruments falls into two categories: calibration which is conducted on a routine basis prior to each use, and periodic, scheduled calibration of instruments and gages against known standards, traceable to the Institute for Environmental Science and Technology (INEST) to ensure the continuing precision and accuracy of such instruments. The calibration policies and procedures set forth in this section apply to all instruments in the latter category, for instant: volume, pressure, vacuum and temperature measurement equipment, balances, pH meters, burette, pipette and so on.

Measuring instrument accuracy is controlled by establishing a preventive maintenance system. Incoming inspections are carried out when instruments are purchased and periodic inspections are carried out during use to check accuracy, calibrate instruments and prevent malfunctions and drops in accuracy.

5.2.2.4. Employee training

Workforce is problem now need to be solved pressingly in the plating companies. Operators that owned of analysis procedure have to train carefully and should have inspection before they can implement analytical process.

For plating bath need to have highest quality, how is operator in small companies can true implementation? This might be considered by inspector and in case, it is difficult for

determine, they should send sample to professional laboratory like University' lab (INEST) or other organizations.

Training program are continuously developed and implemented for all employees performing function that require special instructions. This type training is usually general in its application and required of all employees in the company.

Departments that require a special skill shall implement department specific training. An instructor shall provide the training with reasonable qualifications through either formal training or experience.

All personnel involved in any function effecting data quality (sample collection, analysis, testing, data reduction, and quality control and assurance) will have sufficient training in their appointed position to contribute to the reporting of complete, high quality data.

Quality control training programs will have objectives that:

- Seek solutions to laboratory quality problems
- Instill in all laboratory personnel recognition of the need to continually improve customer'satisfaction with the quality of the laboratory' performance
- Provide all laboratory personnel with the knowledge required in order to carry out management's determination to continually improve its quality performance.

This training objective will help to develop for all laboratory personnel involved in any aspect or function affecting quality, those attitudes, that knowledge, and those skills which will enable each one to contribute to the production of high quality data continuously and effectively.

5.2.2.5. Quality document and records control

The most important elements of the quality assurance program to which document control is applied include:

- Sampling procedures
- Calibration procedures
- Analytical and test procedures
- Data collection and reporting procedures
- Auditing procedures
- Computation and data validation procedures
- The quality assurance manual
- Analytical and testing reports
- Laboratory notebooks
- Corrective action requests

The main reference for analysis of plating solution that Vietnam electroplating companies should use are volumetric (1998) and colorimetric (1999) methods. These books give fully information for analyzing all of spices anions and cations in plating bath.

All files, when is not use will be kept and locked file cabinets. Computer data security will e maintained in accordance with data processing standard operating procedures for restricting entrance to computer data information.

5.2.2.6. Implementing of monitoring and analyzing in effluent control

Equipment to continuously monitor pH should be installed to provide an indication of overall treatment reliability. For larger plants (with discharges of more than 10,000 liters per day), the effluent should be sampled daily for all parameters except metals. Sampling of metals should be carried out at least monthly and when there are process changes. For smaller plants (having discharges of less than 10,000 liters per day), monthly monitoring of all parameters except pH may be acceptable. Fréquent sampling may be required during start-up and upset conditions. Monitoring data should be analyzed and reviewed at regular intervals and compared with the operating standards so that any necessary corrective actions can be taken. Records of monitoring results should be kept in an acceptable format. The records should be reported to the responsible authorities and relevant parties, as required.

5.2.3 Suggestion for effluent control and pollution prevention in electroplating companies in Vietnam

5.2.3.1 Changes in process

- Replace cadmium with high-quality, corrosion-resistant zinc plating. Use cyanide-free systems for zinc plating where appropriate. Where cadmium plating is necessary, use bright chloride, high-alkaline baths, or other alternatives.
- Use trivalent chrome instead of hexavalent chrome; trivalent chromium also rinses more freely and permits simpler waste treatment facilities. There is a slight difference in the colour of the plated metal compared to that plated from hexavalent chromium system. Acceptance of this variation among customers should be promoted by industry itself.
- Give preference to water-based surface-cleaning agents, where feasible, instead of organic cleaning agents, some of which are considered toxic.
- Regenerate acids and other process ingredients whenever feasible.

5.2.3.2 Drag-out minimization techniques

That is the most significant source of chemicals entering the waste stream. By reducing the quantity of dragout, the amount of waste that must be treated and disposed of can be reduced. Therefore, reducing dragout from plating baths not only saves replenishment costs, but also reduces the wastewater treatment cost. Volume of drag-out depends on a combination of factors, including: concentration of chemical in the bath, temperature/viscosity of solution, shape of workpieces, position of workpieces on racks etc. the following solutions can reduce waste releasing in dragout process.

a. Use of lower concentration bath

A reduction in bath concentration can result in a corresponding reduction in chemical loss in drag-out. Process baths should therefore be operated at the lowest possible concentration level without affecting the quality of the product.

Use of a lower concentration of chemicals in the bath reduces the viscosity of the solution. The lower the solution viscosity, the thinner the chemical film clings on the workpieces, which leads to reduced dragout loss.

The bath concentration can be adjusted by reducing the amount of replenishing chemicals gradually until the desired concentration is achieved. Test should be conducted to determine the bath concentration.

b. Bath temperature control

Operating a bath at the upper end of the optimum temperature range, wherever possible, can reduce its solution viscosity. This allows the chemical solution to drain from the workpieces at a faster rate and, therefore, reduces the volume dragout loss.

This technique is limited to baths operating at elevated temperatures and generating no excessive toxic fume. A process bath can also be operated at a higher temperature to increase the evaporation rate of the process solution, and thus offers room for solution replenishment from the dragout tank. This allows dragout reuse and eliminates discharging excess dragout solution.

c. Bath surface tension control

Wetting agents can be added to a process bath to reduce the surface tension of the solution, which can reduce the volume dragout loss. However, different wetting agents have different effects on different baths.

Applicability of this technique depends on the bath chemistries. Excessive amount of these wetting agents may cause foaming problems in the process solution, and may affect the chemistry of the bath itself. Therefore, due care should be taken, through seeking advice from consultants or suppliers, to determine the suitability of this technique and if necessary, to select an appropriate wetting agent.

d. Adequate Drain time

Providing sufficient drain time above the process bath is simplest way of dragout reduction. The longer the workpieces remain above the process bath after emerging from the bath, the lesser will be the volume of dragout.

e. Proper rack design

Apart from facilitating optimal coverage and uniform thickness of metal deposited over the workpieces, proper design of the racks and workpieces and appropriate positioning of the workpieces on the racks can greatly reduce dragout volume due to improved drainage of solution. Figure 5.2 show an example in changing proper rack design

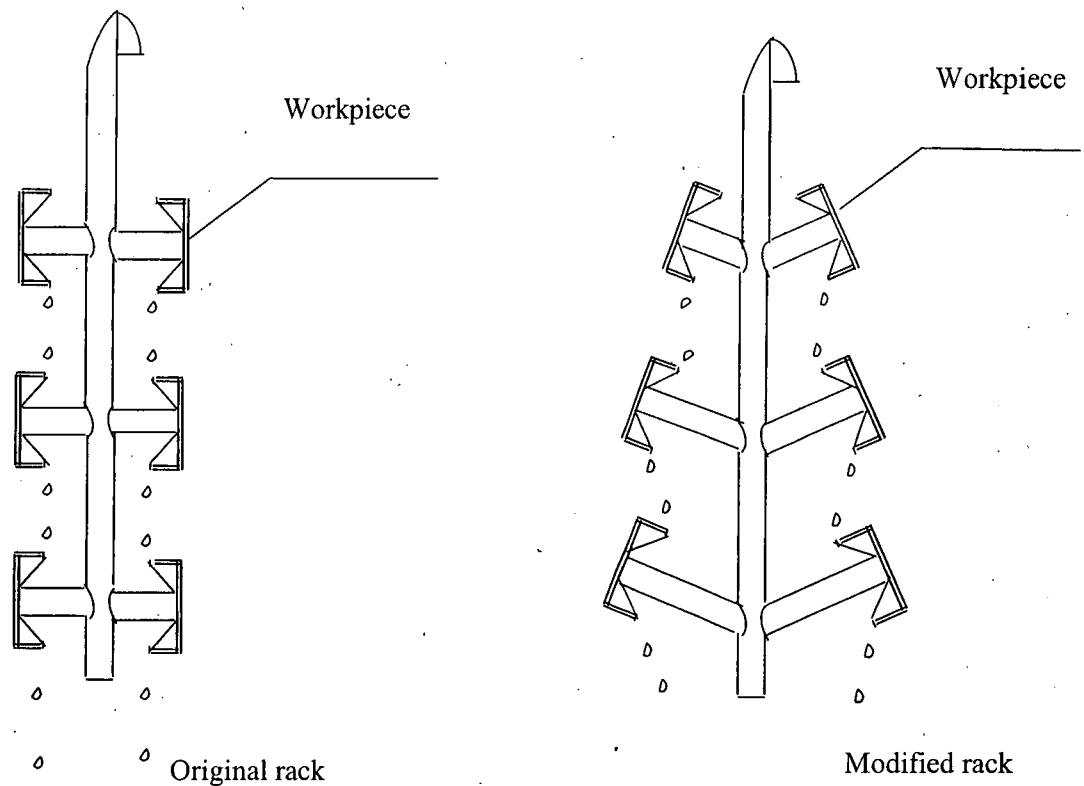


Figure 5.2 Proper rack design

The amount of drag-out loss can be reduced if the workpiece are so oriented that process solution cannot be trapped in grooves or cavities when they are removed from the baths.

Experiment can be implemented in an electroplating company showed that a modified rack for metal boxes can reduce drag-out solution.

g. Use of dragout tanks

Dragout tanks are commonly employed by electroplaters to recover dragout solution. They are “static” rinse tanks prior to the rinse tanks with flowing water. When more and more plated workpiece are rinsed in the dragout tank, the concentration of the dragout tanks solution will increase to the point where it may be returned to the bath to make up for dragout and evaporation losses.

5.2.4. Minimizing water consumption in rinsing system

Rinse water makes up the largest volume of wastewater in electroplating shops and accounts for most of the waste treatment cost. Conserving rinse water not only saves money through reduced water and sewage costs, but also reduces wastewater treatment cost and increases potential for recycling.

There are a number of ways to control water flow and add water on an as-needed basis. The methods for reducing to use rinse wastewater are:

- Reuse of rinse water from one operation as the source for another.
- Cutting off supply when rinse water is no longer required.
- Improving rinsing efficiency.

5.2.4.1. Reactive rinse

Reactive rinse is the reuse of water from one rinsing stage as the source for another. The methods can be used if the reused rinse water has no adverse effect on the product quality.

For example of reuse of water from rinsing showed in figure 5.3. In this method, the water outlet of the rinse tank can be connected to small buffer tank, where the rinse water will be pumped to the other rinse tank by the control of a level sensor.

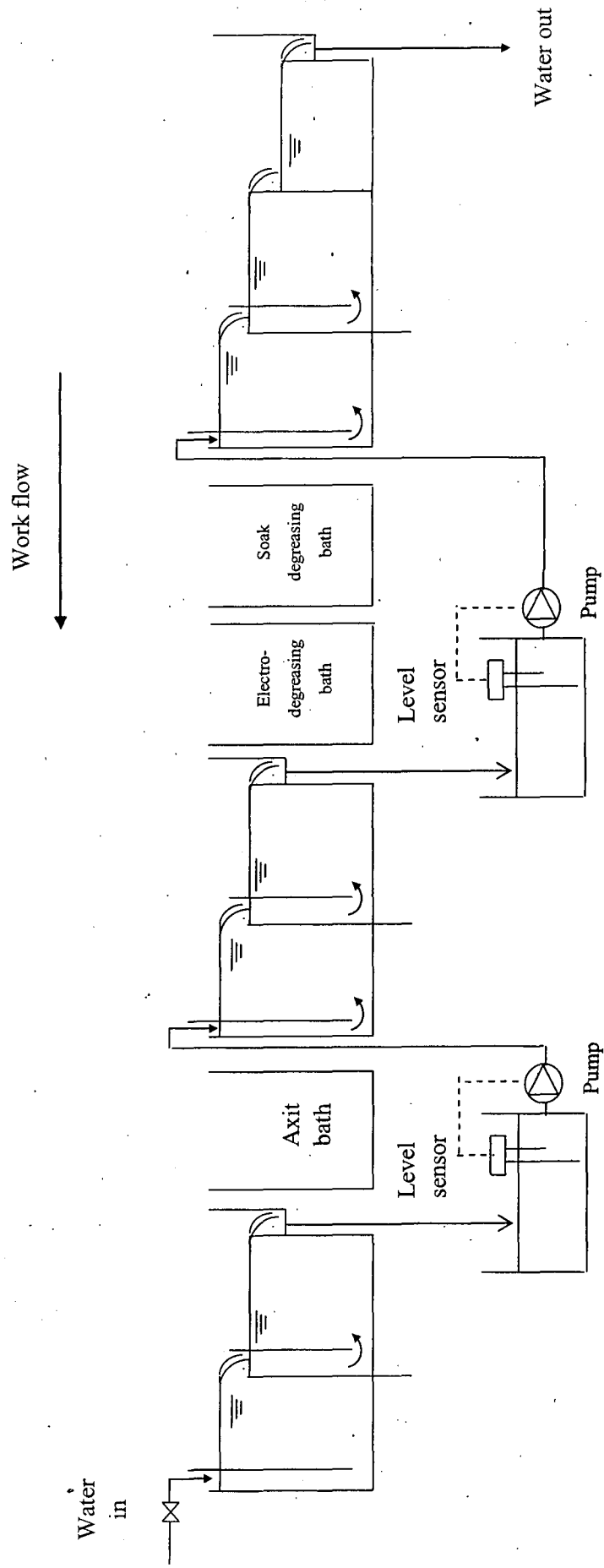


Figure 5.3 Reactive rinse

5.2.4.2. Flow control by restrictor

A flow restrictor is used to regulate the feed rate of fresh water at a constant flow rate despite variations in line pressure and the water faucet setting. It can be used in conjunction with other rinsing techniques to improve water conservation.

Maintaining water flow at a constant flow rate is best suited for production experiencing constant throughput of similar types of products, which therefore requires no frequent adjustment of flow rate. Adequate agitation of the rinsing water should be maintained to enable efficient rinsing.

5.2.4.3. Conductivity controlled rinse

Conductivity control operates on the principle that clean water has a lower conductivity than water contaminated with chemical solutions. This conductivity controlled rinse basically requires a controller, a sensor to detect variation of conductivity of the rinse water, a solenoid valve to control water addition, and an air agitation assembly to provide a thorough mixing of water within each rinse tank. The water supply is cut off by the solenoid valve. When the conductivity sensor detects that the conductivity of the rinse water in the tank exceeds a certain set point value, the controller will open the solenoid valve to feed fresh water, and will close the valve automatically when the conductivity drops below the preset level. The schematic diagram of this technique is given in Figure 5.4.

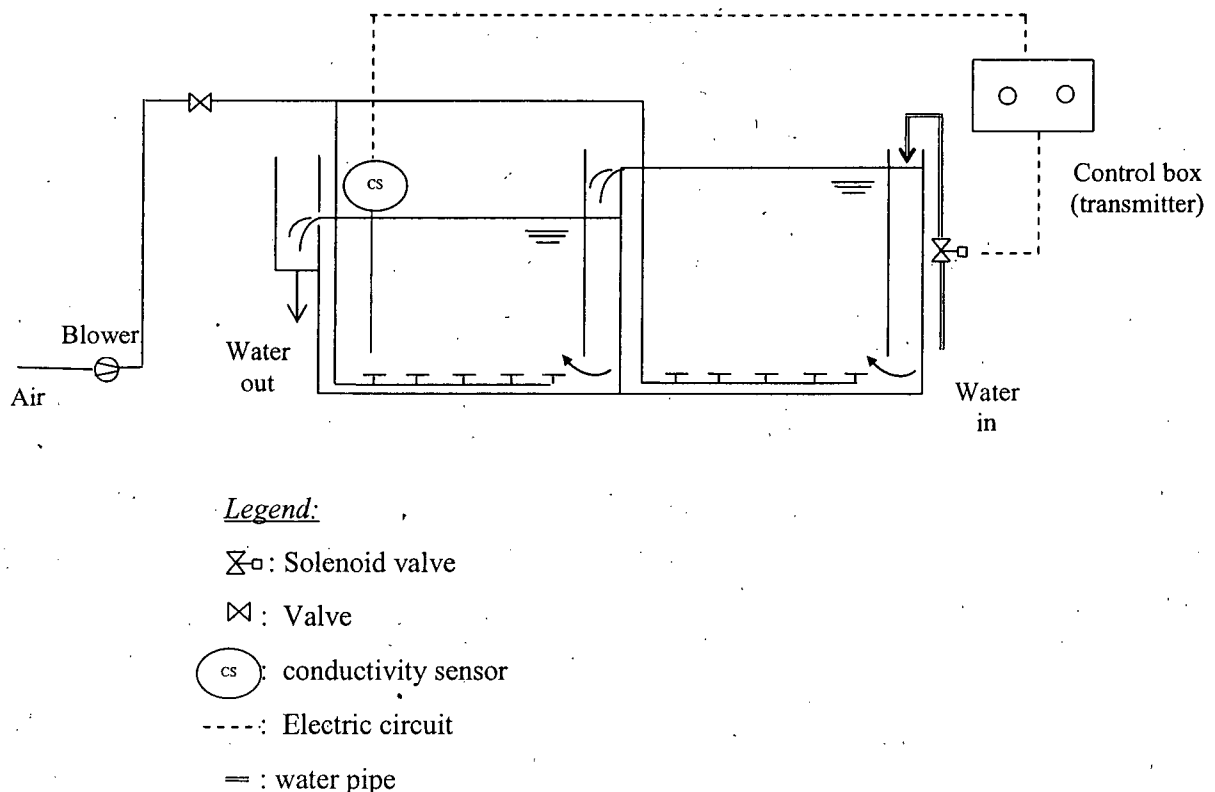


Figure 5.4 Conductivity-controlled rinse (with air-agitation).

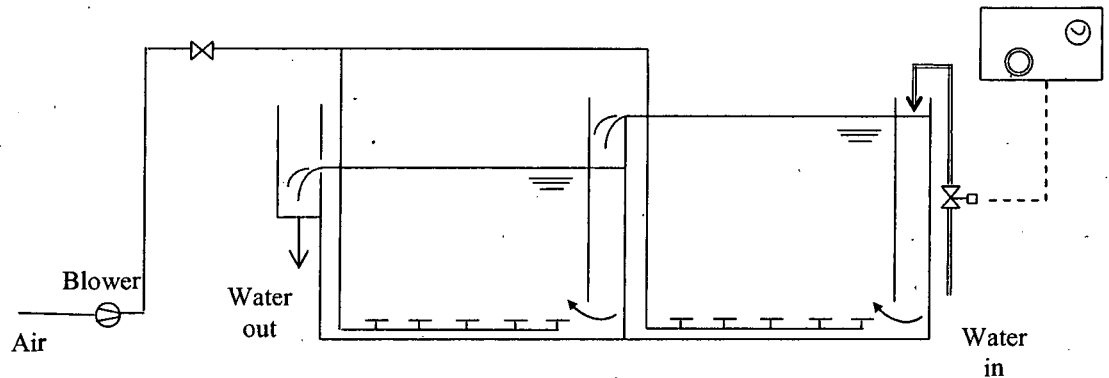
The technique can be easily adopted as the conductivity-controlled system can be simply installed to the existing rinse tank, and the investment cost is comparative low.

This system is best used when the work flow is intermittent. This technique is very suitable for Vietnam plating industry.

Conductivity setting for each plating bath should be determined through on-site tests. For best performance, the sensor probe should be cleaned regularly to avoid deposition of impurities, which may affects its sensitivity.

5.2.4.4. Flow control by timer system

Timer controlled rinse uses a simple device where a timer coupled to a solenoid valve allows fresh water flow for a set period of time, after a switch is activated. After the time period has expired, the valve will be automatically closed loop to stop water flow. The schematic diagram of this system is shown Figure 5.5



Legend:

⊠: Solenoid valve

⊗: Valve

⌚: Time

⊙: Push button

— : water pipe

Figure 5.5 Flow control by timer system

Timer control system can be added to the existing rinsing system to avoid unnecessary waste of rinse water in idle periods when no workpieces are processed. It is most applicable for production lines with an intermittent work flow partner.

5.2.4.5. Improving rinsing effectiveness

Example: can use air agitation is the introduction of clean air into a rinse tank to create a considerable turbulent which greatly improves rinsing effectiveness. Air agitation can be

introduced to existing tanks by the activation of low-pressure blowers or oil-less compressors.

Operation on above equipments does not need high skill operators. These people only educate in a short-time that they can implement easily. Investment cost is not high, place for put equipment smaller than all of others and combinable accessories are very cheap.

5.2.5 Control of air emission

The control of air emission can be approached in several different ways:

- Substitution of less hazardous materials
- Removal of the pollutants form the collected air stream
- Dispersion of the pollutants to acceptable low concentrations
- Exhaust hoods and good ventilation
- Particulate pollutants from mechanical surface preparation can be removed by cyclones or by filters

5.2.6. Cleaner production solutions

This is rather new concept in Vietnam. For electroplating companies, this is nearly not approach. Nowadays, enterprises still think that waste treatment does not bring benefits on economic and it only make increasing fee for production.

Implementation some of cleaner solutions as follow can remarkably improve pollution problems and reduce impact from electroplating industry to environment and human heath. These adoption are not difficult for enterprise, they only have the awareness and good manage plan that mean can be implemented.

1. *Optimizing plan layout*

Optimizing plant layout is important in providing safe working environment and efficient area utilization. Consideration must be given to the positioning of equipment and process controllers, fume extraction, drainage and effluent treatment, chemical and chemical waste storage, and laboratory and QA/QC facilities.

The floor must be waterproof, well drained and resistant to both acids and alkalis. The outlets of rinsing tanks should be directed into drainage gullies or wastewater sumps to keep the floor reasonably dry.

2. *Good housekeeping*

Good house keeping practices include:

- Inventory control

- Material handling and storage
- Material loss prevention
- Process control

3. Staff training and cooperation

The management should adapt training for the industrial staff to the nature of their job duties, the appropriate operating procedures and proper housekeeping practices to minimize waste generation should be taught in training.

Employee co-operation is the key to successful pollution prevention. Personnel whose operation and activities may have impacts on the environment should be encouraged to adopt proper operating procedures according to instruction to minimize environmental impacts. Awards and other forms of incentives can often be effective ways to motivate and boost employee co-operation

4. Management of spill and leaks

The following possible sources of accidental losses should be subject to stringent control and prevention measures:

- Tanks leaks: unprotected steel tanks should be shielded against stray currents with materials such as PVC.
- Solutions remaining in filters, and in bottoms of process tanks should generally be re-used or if this is possible, processed in the effluent treatment plant.
- Equipment leaks: filter, pumps, heat exchangers and their hoses and connections these is properly more loss of chemicals from equipment leaks than any others. An alarm system should be installed on the boiler condensate return line. Periodic examination of the waters should be carried out.
- Over flows: using float level controls
- Accidental opening or rupture of a valve: this problem is best avoided by having no valves at all on the tanks holding concentrated solution. If valve are already installed, they should be sealed off, making them impossible open.
- Spilling of chemicals in handling or in storage, or between process tanks: chemical should be stored by lift trucks in areas safe from damage and sudden flooding.

Wherever possible and practical, a holding pit should be inserted between the plating plant and the discharge to the sewer. Alarm should be installed which automatically sound warnings in case of a sudden change in effluent. These alarms may also shut off the water supply.

5.2. 7 Solutions for Laboratories of Institute at HUT (INEST)

5.2.7.1. *Choose of the analytical methods of chemical substances in plating solutions and effluents*

The INEST laboratories are located in Dai Co Viet Street, Hanoi, and include research and development, technical support and other services, with a staff level approaching university graduate and Master chemists. Laboratories are well equipped with a full range of instruments, AAS, GC/MS and HPLC, UV/visible, polarography and IC, to support research and development and customer services enabling them to cover routine and other analytical investigations.

Considered all of strengths and limitations of each method were given in Chapter 2 along with available instruments, INEST' lab should approach with modern analytical methods. These methods are quickly, accuracy and can determine simultaneously lot elements in a sample. With above equipment, INEST' lab can determine all of cations, anions and even additive organic have present in sample.

For analysis of heavy metal in plating bath and in effluent, INEST has chosen among spectroscopy technique: FAAS should be considered first, second UV/VIS. An Atomic Absorption unit is used for fast and accurate analysis for metal content. This method is nowadays using widely in the world and specified that the most efficient method in analysis of heavy metal in electroplating industry. Technicians constantly monitor and record the ongoing effluent discharge to ensure they meet or exceed required values. Another cause, hence amount of sample is not much every day, detection limit, cost for analysis and implementation is suitable and this method are applicable easily as well, therefore fee for analysing of parameters in plating industry might be accepted by companies.

For determining anions, cations or organic compound both trace and major constituents in plating baths and effluent: Ion chromatography (IC) is an efficient analytical technique that can be used to quickly of a wide variety of electroplating solutions, acid etchants, conversion coatings, cleaning solutions, and the various rinses and wastewaters derived from these solutions. This technique provides a convenient means of quantifying common inorganic anions and cations, certain organic additives, transition metals, polyvalent ions, and organic chelating agents. However, operating cost is rather expensive, addition to it requires the operator have to higher skill and influence factors take play an important significant when employ this instrument. Therefore, the developed methods and the careful research are necessary for technicians of INEST' lab.

Accurate and frequent monitoring of the plating process can result in significant savings due to reduced scrap rate, reduced bath solution losses, and improved device quality. Ion chromatography can also be used for other applications, such as environmental compliance monitoring, quality control of raw material chemicals, and routine sample analysis.

INEST' lab should closely combine with monitoring central if necessary for checking and considering of the companies compliance with environmental law and regulations.

Due to have analytical sufficient facilities as well as good technicians, INEST' lab should help electroplating companies on checking of the companies' analytical results and

comparison with their analysis result. Explain for companies know that where are wrong and how to correct it.

INEST' lab should be the management offices examine as a checking tools, oversee of water quality after treatment in the electroplating companies.

5.2.7.2. Support for electroplating companies on education and technical support

a. Support on education

The availability of College courses leading to technical and Licentiate qualifications that learner can get of the Hanoi University of Technology. Candidates of the electroplating companies seeking qualification would need to comply with requirements for continuous assessment, but those seeking a relevant knowledge base are able to select material for study.

The Institute is always willing to consider proposals for the development of new training programs, providing external funding can be made available to develop the modules/courses etc to help plating companies know how to control process and how to control of chemical substances in plating baths etc.

The possibility of allowing selection of course material relevant to the company' member need is discussed and finally can be decided by director and the group technicians. The Institute has no course available, specific to chemical analysis, but considered that it would be prepared to consider a joint partnership development.

INEST is responsibility for seeing that the require training is made available to person that trained and that records are maintained on each person reflecting satisfactory completion of training program, or qualification tests.

b. Technical and economical assistance

Some specific activations of INEST can support for plating companies as follows:

- Supply for companies information on cost of analysis, chemical and service
- Support of specific guidance on analytical processes for electroplating companies in plating tanks solution and effluent
- Giving Standard procedures for monitoring and measurement for companies
- Introduce trade association (supply chemicals for companies)
- INEST laboratories always combine with plating companies when have projects and theme that sponsored from Government' budget throughout the practical works, INEST' lab can suggest and guide the implemented methods, effectively.
- Electroplating company request routine analytical services can provide solution samples. It is to be noted that proprietary solutions for the industry are quite robust and offer optimum performance over a range of composition. Analytical results for routine work are available to the customer within five days.
- Provision services for companies that not analysis. These companies can be reduced 20%-30% cost for analysis parameters if companies frequently sign analytical contract with INEST.

Assistance of detail problems and improved analytical techniques for charactering plating solutions of INEST for the electroplating companies will help them can aware of their duty obviously and help manufacturers tighten control of process chemistries at once. The result is improved production efficiency and overall profitability. As specifications for plated products become tighter and the cost of producing high-quality products rises, manufacturers need to better understand the critical balances in plating solutions and their impact on the deposit quality.

5.2.8. Government Management Strategy

Pollution problems of electroplating companies are critical causing, this make managers think that how well in monitoring and control efficiency. The owners of enterprise also aware of pollution levels from their companies but they has still not implemented. Companies themselves have a monitoring system and waste treatment do not employ at the moment. Therefore, it better than of all is companies should employ monitoring process and collect samples and they need to be instructed, gradually. These can only employ if having a force the electroplating companies have to comply and perform.

Regulations and policies

- Building the environmental law and regulations: Government should have fully regulations and environmental law: the regulations are obvious, close and especially sensible. In addition to the environmental private standard for plating industry should be promulgated.
- Having policies on Programming, moving and rearrangement all industrial zones
- Building a concentrate area to encourage small and mid-enterprises have stem toxic waste to they can be produced most favorably and easy to treatment waste. At the present time, small plants almost laid insert with population areas and waste untreated so these solutions are really necessary and pressing.
- Effect of management tools should be improved and obligated
- Implementing analytical methods and should approach with modern ones
- Guidance on legislation, health and safety, environmental support to each company. Implementation should be constantly maintained monthly or annually.
- Government should have a survey about analytical status and effluent control at present time in the electroplating companies in Vietnam. Since then give appropriate solutions and timely decisions
- A quality policy is established and communicated throughout the company

Afterwards, government should establish an industrial support network, and the use of private Web to support training for the electroplating industry.

Financial assistance and applying economical tools

Government should have assistance policy for enterprises that have to move another place; furthermore, they have to change new technology and build waste treatment system to make less pollution waste.

Having many specific assistance solutions such as: enterprises can be loaned with interest rate specially, reduced tax and easier with import policies...

Government should apply more encourage solutions for small companies, that can gather them become an association. Implementation of process control (especially in the analytical process control) to meet a part of QA will be discussed and planned by these companies. Companies will assist together in order to employ. Government encourage co-operation between different companies will create an interest and more easily in implementation. Monitoring and effluent control can be given by environmental managers of each company. Process and monitoring time will be easily adopted by a big laboratory of the gathered companies.

Othermore, effluent control also is implemented by association companies. Government has to have satisfactory award policies for companies which treated wastewater can achieve the environmental standard and always comply with environmental regulations.

Government should apply policies to offer award for companies that have complied correctively the environmental law and simultaneously penalize for companies do not aware to implement.

Besides, for self-aware companies have implemented environmental law or invested on equipment innovation in order to reduce environmental pollution, that is, government should encourage policies as reducing turnover tax and income tax or they can be borrowed with priority loan interest.

Government can regulate about cost for analyzing chemical substances for the electroplating companies depend on their economical condition

Technical solutions

Government, industry and professional association and Scientifics should enhance technology transfer. Continued government-industrial partnerships and Government should conducts for the electroplating companies the experiences and treatment technologies of developed countries as Switzerland (recovery, recycle, energy saving etc.)

Training course organization frequently for technical staff working is analytical basic skills in the plating industry.

Put in place a system to monitor and disseminate development in analytical science on an on-going basis so as to ensure a regular review of the plating industry's requirements. This will help to maintain and hopefully enhance the industry's impact and competitiveness via quality control of processes and products.

Assistance for the electroplating plants about technique and the solutions to treat wastes due to in fact, all small plants lack of information in technical and chemical safety, occupational disease and treatment waste. Having good co-operation with professional analytical chemists to produce the best possible material.

For larger companies that have just invested in less waste production line, government have to force using continuously of production line less waste to reduce waste sources causing environmental pollution.

- Should continue to enhance encourage the electroplating companies perform on life-cycle assessment, ISO 14000, QA system.

For backward technology companies

These companies have to be assessed and audited cleaner production for each one improving gradually.

For small companies, government should step by step give a sensible process within have closely observation of the specific function offices as:

- Having management organizations come in to each precinct/commune
- Companies must have period reports about active status both production and environmental status.
- Frequently having inspection on the companies' practical status. If any companies do not assure production conditions as in commitment, then administrative will decide a resolute treatment depends on the break levels.
- Government should concentrate small companies to make an association so he can easier to manage.
- For companies that they correctly implemented commitments or installed modern equipment for waste treatment, government have to encourage, timely and even may propose for reduction tax, create good conditions for consuming products.
- Training programs are established and documented frequently for the operation who implemented on analytical process control and effluent control.

Having an environmental agreement for every company and compel with them that they have to install equipment on pollution source treatment although it is really simple. (Inclusive gas waste).

Conclusions

After six month's implementation of master thesis: "*Description and Assessment of analytical methods for determination of chemical Substances in plating baths and Waste water for environmental Monitoring and quality Assurance*" the results were received includes:

- Overview of electroplating industry, this will provide a viable reference for operator/owner best knows their facilities and processes, impacts to environment stemming from electroplating industry therefore should able to make the appropriate decision.
- Thesis specified environmental status of electroplating industry in Hanoi, Vietnam along with waste characteristic and environmental impact stemming from it through data that collected from some reports in 1997, 1998, 1999, 2001, 2003.
- Description and appreciation on methods of analysis of chemical substances in plating bath and effluent can applicable in the electroplating industry (assessment advantages and disadvantages of each method, detection limit, operating cost and investment cost for instrument etc.). In addition provided some information on analytical status of countries in the world (USA, Switzerland) and Vietnam. Tendency of the countries in the world in the analytical performance of chemical substances in the electroplating industry.
- Methods for effluent control, and pollution prevention which have been applying in developed countries. Assessment of each method strengthen and limitation. Status of effluent controls and pollution prevention in the electroplating companies in Vietnam.
- Analysis of benefits when employing effluent control, analyzing process control in bath solution.
- Suggestion of appropriate methods for analysis of chemical substances for Vietnam electroplating companies. Given the analytical procedure control in order to reach perfection quality requirement. This process also take plays an important part in quality assurance system.
- Suggestion of the analytical methods for INEST, co-operation between INEST and the electroplating companies in Vietnam, supporting solutions of INEST for electroplating companies in Vietnam.
- Suggestion of the detail management strategy of Government for the electroplating companies.
- Provide some cleaner production solutions for enterprises.

In summary, the master thesis complied with information from reports, articles, books, guides, web pages. The thesis' primary purpose are to assist Vietnam electroplating companies find correctly methods in the analytical process control, effluent control. In

addition the master theses also provide methods for analysis of chemical substance in plating solutions and effluents that are most suitable for the electroplating company' conditions in Vietnam. Furthermore, the detail suggestions are applicable for Government and for INEST' lab (at HUT) these will help for the decision – maker find out the accuracy management solutions, give timely decision to assist and decide the detail solutions that can be applied for each electroplating company. Good implementation all above solutions, the electroplating companies in Vietnam adopted a basically part of quality assurance and environmental management system, improve significant quality of product and meet the customer' requirement and the environmental protection.

Consequently, considering all-sized, need to combine between the environmental management organizations and the plants as well as scientifics in order to give environmental standards and regulation are both more specific and sensible way. All of these will create sustainable development for the economy in general and electroplating plants in particular

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Annexes

Annex 1.1 List of Law and Regulation Related to Environment in Vietnam

1. Primary Legislation on Environment

- ❖ Environmental Protection Law 1994
- ❖ Decree on Guiding Implementation for Environmental Protection Law (Gov. Decree No. 175-CP, 1994)
- ❖ Decree on Sanction for Administrative Violations for Environmental Protection Law (Gov. Decree No.26-CP, 1996)
- ❖ Decree No. 22/CP on Responsibilities, Authority and Organisation of the Ministry of Science, Technology and Environment (22 May, 1993)
- ❖ Instructions on Strengthening Environmental Protection in the period of Industrialization and Modernization (No. 36-CT/TW, 1998, Vietnam Communist Party)

2. Specific Legislation on Environment

(1) Pollution control

- ❖ Air Quality, Ambient Standards (TCVN 5937, 1995)
- ❖ Air Quality, Hazardous Substance Standards (TCVN 5938, 1995)
- ❖ Air Quality, Industrial Standards for Inorganic Substances (TCVN 5939, 1995)
- ❖ Air Quality, Industrial Standards for Organic Substances (TCVN 5940, 1995)
- ❖ Standards for Noise in Public and Residential Areas (TCVN5945, 1995)
- ❖ Standards for Noise on Road Motor Vehicle (TCVN5948, 1995)
- ❖ Soil Quality Standards on Pesticide Residue Limits (TCVN5941, 1995)
- ❖ Industrial Waste Water Discharge Standards (TCVN5945, 1995)
- ❖ Water Quality Standards; Coastal Water (TCVN5943, 1995)
- ❖ Water Quality Standards; Groundwater (TCVN5944, 1995)
- ❖ Water Quality Standards; Surface Water (TCVN5942, 1995)

(2) Nature conservation

- ❖ Law on Forest Protection and Development (12 August 1991)
- ❖ Regulations on management regulations for production forests, protection forests and Special-use
- ❖ Forests: attached to Decision No. 1171/QD (November 1986)
- ❖ Decree on endangered species and management and conservation mechanisms (No. 18/HDBT, 17 January 1992)
- ❖ Decision on use of open land, bare hills, forest, coastal alluviums and water bodies (No. 327/CT, 15 September 1992)

- ❖ Directive on protection and management of endangered plant and animal species (No. 130/TTg, 27 March 1993)
- ❖ Directive on urgent measures to protect and develop wild animal species (No. 359/TTg, 29 May 1996)
- ❖ Official Letter on strengthening wildlife protection and development (No. 2472/NN-KL-CV, 24 July 1996)
- ❖ Decree on allocation and lease of forest land to organisations, households and individuals for long-term forestry purposes (163/ND-CP, 16 November 1999)
- ❖ Decision on the management of Special-Use Forest, protection forest and production forest (No. 08/QDTTg, 11 January 2001)

(3) *Environmental Impact Assessment (EIA)*

- ❖ EIA and Licensing, Decision on Regulations and Appraisal Council (MOSTE Decision No. 1806/QDMTg, 1994)
- ❖ EIA and Licensing, Regulations and Appraisal Council (MOSTE Decision No. 1807/QD-MTg, 1994)
- ❖ EIA Instruction for Guiding Operating Units (MOSTE Instr. No.1420/QD-MTg, 1994)
- ❖ EIA Instruction for Report to the Direct Foreign Investment Project (MOSTE Instr. No. 715/QD-MTg, 1995)
- ❖ Temporary Guidance for Environmental Impact Assessment of Technical-Economic Project, No.1485/MTg, 1993
- ❖ Circulation No. 490/1998/TT-BKHCMNT, MOSTE, Guiding the Preparation and Evaluation of AEI (EIA) Reports for Investment Projects

(4) *Others*

- ❖ Law on Water Resources (January 1999)
- ❖ Law on Minerals (20 March 1996)
- ❖ Law on Fishery (draft)
- ❖ Law on Land, 1993
- ❖ Decree No. 22/1998/ND-CP (Compensation for lost property by State's expropriation)
- ❖ Circulation No. 145/1998/TT-BTC, Guidelines on the Implementation of the Decree 22/1998/ND-CP, Ministry of Finance (Extracts)
- ❖ Master Guidelines and Policies to Utilize Unoccupied Land, "Barren", Hilly Areas, Forests, Denuded, Beaches and Waterfront (COM Decree No. 327, 1992)

Annex 1.2. industrial wastewater discharge standard TCVN 5945-1995

1. Scope

1.1 This standard specifies limit values of parameters and concentration of substances in industrial waste water.

In this standard **industrial waste water** means: liquid water or waste water produced by reason of working or production processes taking place at any industrial, servicing and trading premises, etc.

1.2 This standard is applied to control of quality of industrial waste waters before being discharged into a water body.

Water body means: inland water, include any reservoir, pond, lake, river, stream, canal, drain, spring or well, any part of the sea abutting on the foreshore, and any other body of natural or artificial surface or subsurface water.

2. Limitation Values

2.1 Values of parameters and maximum allowable concentrations of substances in industrial waste waters before being discharged into water bodies are shown in the table 1.

2.2 Discharge standards applying for waste waters produced by specific industry such as paper, textile or oil industries are specified in a separate standard, respectively.

2.3 Industrial waste waters containing the values of parameters and concentrations of substances which are equal to or lower than the values specified in the column A (table 1) may be discharged into the water bodies using for sources of domestic water supply.

2.4 Industrial waste waters containing the values of parameters and concentration of substances which are lower than or equal to those specified in the column B (table 1) are discharged only into the water bodies using for navigation, irrigation purposes or for bathing, aquatic breeding and cultivation, etc.

2.5 Industrial waste waters containing the values of parameters and concentrations of substances which are greater than those specified in the column B but not exceeding those specified in the column C (table 1) are discharged only into specific water bodies permitted by authority agencies.

2.6 Industrial waste water co

ntaining the values of parameters and concentrations of substances which are greater than those specified in the column C (table 1) shall not be discharged into surroundings.

2.7 Standard methods of analysis of parameters and concentration of substances in industrial waste waters are specified in available current TCVN.

Table 1 Vietnam Standard 5945-1995

Industrial waste water discharge standards. Limit values of parameters and maximum allowable concentration of pollutants

No	Parameters	Unit	Limit		
			A	B	C
1	Temperature	°C	40	40	40
2	pH		6-9	5.5-9	5-9
3	BOD5	mg/l	20	50	100
4	COD	mg/l	50	100	400
5	Suspended solids	mg/l	50	100	200
6	Ashen	mg/l	0.05	0.1	0.5
7	Cadmium	mg/l	0.01	0.02	0.5
8	Lead	mg/l	0.1	0.5	1
9	Clo spur	mg/l	1	2	2
10	Cr (VI)	mg/l	0.05	0.1	0.5
11	Cr (III)	mg/l	0.2	1	2
12	Mineral oil and fat	mg/l	Not detect	1	5
13	Animal-vegetable fat and oil	mg/l	5	10	30
14	Copper	mg/l	0.2	1	5
15	Zinc	mg/l	1	2	5
16	Mn	mg/l	0.2	1	5
17	Nickel	mg/l	0.2	1	2
18	Organic phosphorous	mg/l	0.2	0.5	1
19	Total phosphorous	mg/l	4	6	9
20	Iron	mg/l	1	5	10
21	Tin	mg/l	0.2	1	5
22	Tetrachlorethylene	mg/l	0.02	0.1	0.1
23	Mercury	mg/l	0.005	0.005	0.01
24	Total nitrogen	mg/l	30	60	60
25	Trichloroethylene	mg/l	0.05	0.3	0.3
26	Ammonia (asN)	mg/l	0.1	1	10
27	Fluoride	mg/l	1	2	5
28	Phenol	mg/l	0.001	0.05	1
29	Sunfur	mg/l	0.2	0.5	1
30	CN	mg/l	0.05	0.1	0.2
31	Gross α activity	Bq	0.1	0.1	-
32	Gross β activity	Bq	1.0	1.0	-
33	Coliform	MPN/100 ml	5000	10000	-

Annex 1.3. Industrial wastewater discharge standard of some developed countries

Parameter	Discharge Values (mg/l)		
	Sweden	France	USA (daily max)
Cadmium	0.1	0.2	0.11
Chromium (total)	1	2	2.77
Chromium (Hexavalent)	0.1	0.1	-
Cyanide (free)	0.1	0.1	0.86
Cyanide (Total)	1	1.2	-
Copper	1	2	3.3
Lead	1	0.2	0.6
Zinc	2	5	2.6
Nickel	1	5	3.98
Tin	1	2	
Silver	1		0.43
Iron	2	5	-
Aluminum	2	5	-
Fluorides	-	5	-
Oil	-	5	-
Suspended matter	10	15	60
COD	-	150	-
pH range	-	6.5-9	6-9

Annex 1.4. Discharge standard of industrial wastewater of Thailand

Items	Units	Standard values	Remarks
BOD (5 days, at 20°C)	mg/l	20-60	
SS		Depend on dilution ratios of wastewater and receiving water	Ratio: 1/8 to 1/150 Max 30 1/151 to 1/300 Max 60 1/301 to 1/500 Max 150
Disolved solids (DS)	-	Max 2000 or under office's consideration but not more than 3,000	If salinity of receiving water is higher than 2,000 mg/l, DS in the effluent should not be higher than 5,000 mg/l of the DS in the receiving water
pH	-	5 - 9	
Permanganate value	mg/l	Max.60	
Sulphide (as H ₂ S)	-	Max 1.0	
Cyanide (as HCN)	-	Max. 0.2	
Oil and grease	-	Max 5.0	Refinery & lubricant oil Max 15.0
Formaldehyde	-	Max 1.0	
Free chlorine	-	Max 1.0	
Temperature	°C	Under 40	
Heavy metals			
Zinc	mg/l	Max 5.0	Zinc industry Max 3.0
Chromium (Cr)	-	Max 0.5	Zinc industry Max 0.2
Arsenic (As)	-	Max 0.25	
Copper (Cu)	-	Max 1.0	
Mercury	-	Max 0.005	Zinc industry Max 0.002
Cadimium	-	Max 0.03	Zinc industry Max 0.1
Barium (Ba)	-	Max 1.0	
Selenium	-	Max 0.02	
Lead	-	Max 0.2	
Nickel	-	Max 0.2	Zinc industry Max 0.2
Mangane	-	Max 5.0	
Silver	-		Zinc industry Max 0.02

Annex 1.5. Sewer discharge limits in selected countries

Parameter	Discharge limits of Sewer system (mg/l)			
	Baden Württemberg (FRG)	Melbourne (Australia)	Italy	Singapore
Cadimium	1	10	0.02	1
Chromium (total)	2	10	4	5
Chromium (Hexavalent)	0.5	0.2	-	-
Cyanide	0.2	1	2	
Copper	2	10	0.4	5
Lead	2	10	0.3	5
Zinc	5	10	1	10
Nickel	3	10	4	10
Tin	5	10	-	-
Silver	1	2	-	-
Iron	10	30	4	50
Aluminium	10	-	-	-
Sulfides	10	1	-	-
Sulphates	400	300	-	-
Oil&Grease	100	200	-	-
Phenols	100	100	-	-
pH	6-9.5	6-10	5.5-9.5	6-9
Temperature max	35°C	-	-	-