



CHAPTER V

CONCLUSION AND RECOMMENDATION

In this study, cadmium, copper, lead, mercury, and zinc are of interest due to their toxicities and their existences in trace amounts in air particulates. Since anodic stripping voltammetry and atomic absorption spectrophotometry offered the required sensitivity, availability, simplicity, and capability of multielement analysis, both techniques were used for analyses of these metal species.

A glassy carbon electrode mercury plated "in situ" which was proved to be more sensitive than the glassy carbon electrode itself was used throughout the anodic stripping voltammetric study of these metal species, except mercury the glassy carbon electrode was used instead. The anodic stripping analyses of Cd(II), Cu(II), and Pb(II) species were performed in $5.0 \mu\text{g}/\text{cm}^3$ of Hg(II) and 0.1 M KNO_3 solution by deposition at the potential of -0.80V for 20 minutes and anodic scanning with the rate of $0.8 \text{ V}/\text{minute}$. A linear dependence of the anodic stripping peak current of each metal species on its concentration was obtained in the concentration range $5.0 - 100.0 \text{ ng}/\text{cm}^3$. The anodic stripping analysis of Hg(II) species was performed in 0.1 M KNO_3 at pH 2 by deposition at the potential of $+0.10\text{V}$

for 20 minutes and anodic scanning with the rate of 0.8 V/minute. A linear dependence of the anodic stripping peak current of Hg(II) on its concentration was achieved in the concentration range of 100.0 - 1000.0 ng/cm³. The anodic stripping analysis of Zn(II) species was performed in 5.0 µg/cm³ of Hg(II) and acetate buffer pH 5.8 by deposition at the potential of -1.40 V for 20 minutes and scan rate of 0.8 V/minute. A linear dependence of the anodic stripping peak current of Zn(II) on its concentration was also obtained in the concentration range 10.0 - 100.0 ng/cm³. The summary of cathodic peak potentials and anodic stripping peak potentials of these metal species are presented in Table 34.

Corresponding to the intermetallic formation between copper and zinc in the mercury film, the anodic stripping analysis of Zn(II) species was separately performed and the anodic stripping analysis of Hg(II) was firstly determined, then the Cd(II), Cu(II), and Pb(II) were simultaneously analyzed. A simultaneous analysis of Cd(II), Cu(II), and Pb(II) species using anodic stripping voltammetry was studied in 5.0 µg/cm³ of Hg(II) and 0.1 M KNO₃ solution by deposition at the potential of -0.80V for 20 minutes and scan rate of 0.8 V/minute. Two mixture solutions containing 0.- 20.0 ng/cm³ of Cd(II), 0 - 49.0 ng/cm³ of Cu(II), 0 - 30.0 ng/cm³ of Pb(II), 0 - 50.0 ng/cm³ of Zn(II) species in 5.0 µg/cm³ of Hg(II) and 0.1 M KNO₃ were analyzed by standard addition technique.

Table 34 Cathodic peak potentials and anodic stripping peak potentials of the metal species understudied.

Metal specie	Supporting electrolyte	$E_{p,c}$ (V)	$E_{p,a}$ (V)
Cd(II)	0.1 M KNO_3	-0.73	-0.68
Cu(II)	0.1 M KNO_3	-0.10	+0.05
Hg(II)	0.1 M KNO_3	+0.10	+0.25
Ga(III)	Acetate buffer pH 5.8	P	-0.95
Pb(II)	0.1 M KNO_3	-0.55	-0.50
Zn(II)	Acetate buffer pH 5.8	-1.20	-1.10

P No peak observed

The results indicated the maximum errors of 5.0 % for Cd(II), 4.5 % for Cu(II), and 3.6 % for Pb(II) species.

Since the formation of copper - zinc intermetallic compound could overcome by addition of an excess of gallium to form gallium - copper instead, the molar ratio of Ga(III) to Cu(II) for this compound under conditions of study was found to be 2 : 1 for Ga(III) to Cu(II) species. The effect of Ga(III) concentration on the anodic stripping peak current of Zn(II) in the mixtures was also studied. The anodic stripping peak current of Zn(II) reached a constant value when the molar ratio of Ga(III) to Cu(II) was more than 140:1 . Therefore, the molar ratio of Ga(III) to Cu(II) as 200:1 was used to calculate the added gallium and the concentration of Ga(III) as $10.0 \mu\text{g}/\text{cm}^3$ was added to all samples. The concentrations of Zn(II) species in the mixtures of Cd(II), Cu(II), Hg(II), and Pb(II) were determined by standard addition method. The maximum error obtained for these determinations was 4.6 % .

In order to analyze Cd(II), Cu(II), Pb(II), and Zn(II) species by atomic absorption technique. The study of the relationships between the absorbances and the concentrations of each metal species in both the single metal ion solution and the mixture of these metal species were examined. It resulted in a linear relationship for the single metal ion solution of Cd(II), Cu(II), Pb(II),

and Zn(II) species in the range of 0.1 - 3.0 $\mu\text{g}/\text{cm}^3$. However, when the concentration of each metal species in the mixture exceeded 1.0 $\mu\text{g}/\text{cm}^3$, the linear relationship was no longer obtained. The Hg(II) species was determined by flameless atomic absorption and the amount of mercury was directly read from the instrument. The concentration effect of other metal species in the mixture on the absorbance for determining mercury was also studied. The results implied that no interference was observed for the determination of mercury in the presence of Cd(II), Cu(II), Pb(II), and Zn(II) species in the concentration range of 0.3 - 2.0 $\mu\text{g}/\text{cm}^3$.

Both anodic stripping voltammetric and atomic absorption spectrophotometric techniques were used to determine Cd(II), Cu(II), Pb(II), Hg(II), and Zn(II) species in air particulates. The air particulate samples were collected on Millipore membrane by means of a Bendix Telematic Air Sampler. The sampling areas are Patumwan, Ratchaprasong, Chit Lom, Phloenchit, Sukhumvit soi 10, and Sukhumvit soi 21. A total of 24 samples were obtained.

The air particulate samples were decomposed by digesting with concentrated nitric acid and heated to aid the dissolution.

The samples were diluted with double deionized water to the exact volumes. Then, an aliquot of the sample solution was subjected to anodic stripping analysis (ASV)

and an other aliquot was analyzed by atomic absorption spectrophotometric technique (AAS) for cadmium, copper, mercury, lead, and zinc as described conditions.

The amounts of metal species in air particulate samples understudied, did not vary markedly from station to station, and from either method for each station. The ranges of metal contents in air particulates by ASV and AAS methods are given in Table 35. The distribution of trace heavy metals in air particulates mainly arised from the exhaust emissions of the motor-vehicles, which included fuel-oil, lubricants, and the wear metals of them. Minor contribution came from local industrial contamination. Although , there is no ligislation controlling the amounts of trace metals presented in ambient air in Thailand, these results may provided some baselines for the establishment of the standard values of trace metals in ambient air. The higher sensitivity for anodic stripping technique can be achieved by using the modified excitation wave form such as differential pulse and by using rotating glassy carbon electrode electrode mercury plated "in situ" . These should be attempted for further study. For atomic absorption technique, the nonflame atomic absorption is usually found to be more sensitive than flame atomic absorption and the smaller volume of solution required for nonflame atomic absorption. These techniques may be interesting for study of trace metals in the environmetal sample.

Table 35 Ranges of metal contents in air particulates
by ASV and AAS methods

Metal	Content* ($\mu\text{g}/\text{m}^3$)	
	ASV	AAS
Cadmium	n - 5.26 ± 0.14	n - 6.20 ± 0
Copper	n - 23.15 ± 1.02	n - 19.94 ± 0
Lead	$0.60 \pm 0.20 - 47.25 \pm 1.64$	n - 46.21 ± 1.73
Mercury	n	n - 5.94 ± 0.19
Zinc	n - 15.70 ± 0.32	n - 17.32 ± 1.20

* average \pm mean deviation of 3 trials

n undetectable