

CHAPTER V

DISCUSSION

Solvent extraction method investigated in this study is the APDC-MIBK Extraction System follows by back extraction with 4N nitric acid. The investigation of several experimental conditions affecting the efficiency of the extraction system are tested step by step in the first extraction of Cu, Ni, Pb and Zn and in back extraction. The improved solvent extraction method is, then, validated with the Certified Reference Materials which are prepared by the National Research Council of Canada.

APDC, normally, will decompose in the aqueous solution this is because it is a monobasic (99). When it is added into the sample in which the pH is adjusted to acid for the purpose of preservation of the sample before analysis. Therefore, it should rapidly decompose upon addition making the undecomposed APDC, if any, to be insufficient to form complexes with the metals. Therefore, the pH adjustment of sample before adding the chelating agent, APDC, is the best way to prevent the decomposition of APDC. From the results of this study it showed that, for the first extraction of interested metals, the pH adjustment of treated seawater sample before adding the chelating agent, 2% APDC, and organic solvent, MIBK, is the appropriate sequence because it gives the best percentage extraction of more than 96 % and 4 min-shaking time is sufficient to ensure complete or nearly complete extraction of the metal-complexes confirming the results

obtained by Guardia and Vidal (81). The minimum quantity of APDC which gives the complete extraction of interested metals (higher than 99 %) is 5 ml of 2 % (w/v) APDC : 100 ml treated sea water sample which is sufficient for extracting the seawater, having the metal concentration of not more 5 ppb. In all cases, the chelating solution should be freshly prepared. By comparing the shaking time on back extraction by 4 N nitric acid from MIBK, chloroform, Freon TF and carbon tetrachloride, which are the widely used organic solvents in solvent extraction, the shaking time for the back extraction of metals from chloroform and Freon TF are longer than MIBK. Magnusson and Westerlund (48) found that the shaking time for the back extraction of Cu, Cd, Ni, Pb and Zn from Freon TF was 30 min and 24 hours for Cu only if chloroform was used as organic solvent. As for MIBK, the back extraction proceeded more rapidly than chloroform and Freon TF. Furthermore, chloroform and carbon tetrachloride are known to be possible carcinogen (47). The less toxic organic solvent, Freon TF, has a weak, innocuous odour and is expensive but the only drawback is the low solubility of metal complex in Freon TF comparing to chloroform (47). Taking these factors into consideration, MIBK is the most suitable for the APDC-MIBK extraction method. From this study, the optimum volume of MIBK which yields more than 90% of extracted metals is 5 ml. 5 ml of MIBK gives the extraction ratio, $V_{aqu.}/V_{org.}$, around 20 and distribution ratio between 100 to 200.

Cu is quantitatively extracted at pH value from 2.5 to 5, which gives the percentage extraction of Cu from 99 % to 89 % respectively. The pH value suitable for Ni extraction is from 2-6 (the percentage extraction varies from 100 % to 91 %) while pH from 4-

8 give the percentage extraction from 99 % to 92 % for Pb. Zn is best extracted at pH from 4-8 and has the percentage extraction from 97 % to 100 %. In order to quantitatively extract the four metals (Cu, Ni, Pb and Zn) from seawater sample in single extraction by the improved solvent extraction method, the pH of the aqueous phase (sample) should be adjusted to the pH range 4-6. Since APDC is the monobasic when undergo decomposition in aqueous solution and below pH 2 the rate of decomposition of APDC is no longer pH dependent, therefore, the extraction efficiency drops rapidly (<10% at pH 1.5) and subsequently to 0.0% at pH 1.0 because of the decomposition of APDC in an acidic medium as reported by Newland and Clements (82). The stability constant ($\log K$) of dithiocarbamate complexes in organic medium of Zn^{2+} , Ni^{2+} and Pb^{2+} are 9.8 - 10.4, 13.2 and 10.8 respectively (100). According to the sequence of stability of transition metal complexes, which was set by Irving and Williams (101), therefore, the stability constant of dithiocarbamate of Cu^{2+} will lie between 10.8 - 13.2. Thus, Ni^{2+} will firstly form complex with APDC follow by Cu^{2+} . Zn^{2+} and Pb^{2+} will form complexes with APDC almost the same time after Ni^{2+} and Cu^{2+} are complexed. The extracted metal complexes (Cu, Ni, Pb and Zn) remain stable in the MIBK for at least one day (13,77). Therefore, as long as the first extraction and back extraction are carried out in the same day, no problem will arise due to the decomposition of metal chelates in MIBK.

For back extraction by nitric acid, the effective strength of nitric acid and the shaking time for extraction are 5 ml 4 N nitric acid and 5 min-shaking time respectively. For the stability of the analytes (Cu, Ni, Pb and Zn) in the acid extract (4 N nitric acid),

some amount of the analytes in nitric acid might be lost due to the adsorption on container wall (12-19) during the storage period of stability studied. The concentration of Cu stabilizes for at least 2-4 weeks. From the fourth weeks onward, it slightly decreases from 100 % to 91.75 % and reaches 58.1% in the ninth week. The concentration of Ni decreases from 100% to 95.84 % within two weeks and decreases to 26.46 % in the ninth week. The stability of Pb is the same as Ni in which the concentration of Pb decreases to 91 % from the original concentration in the acid extract in the second week and finally decreases to 8.25 % in the ninth week. The concentration of Zn slightly decreases from 100 % to 93 % after 4 weeks in 4 N nitric acid but Zn remains stable for a longer period better than Ni, Pb and Cu. From Jan and Young (46) the stability of Cu is also the same as this studied but for Ni, Pb and Zn, their stabilities are only one week which are less than the results of this studied. In summary, the stability times of Zn and Cu are 9 weeks and 3 weeks and Ni and Pb are 2 weeks in acid extract respectively. These stability times of the analytes in 4 N nitric acid are longer than in MIBK. Thus, it is better to back extract the metals (Cu, Ni, Pb and Zn) by acid, nitric acid in particular (48) acids. The reason why the concentrations of the analytes in 4N nitric become lower during the storage period of studying, it may be happened either by the loss of analytes from nitric acid onto the surface of container wall by the adsorption process (12-19, 31,33) or probably by the changing of analytes into unmeasurable form by AAS. Although the storage of the metals in samples at $\text{pH} < 1.6$ is the widely practice for stabilizing trace metals species in acid extracts, it is advisable to determine the optimum conditions for a particular metal (102). Therefore, more

should be investigated in the method of stabilizing metals in acid extracts.

Because of the limited amount of certified reference materials available for validating the Improved APDC-MIBK Extraction Method followed by Back Extraction with 4 N nitric acid, therefore, the validation of method can be done only once. The analytical results of Cu, Ni, Pb and Zn seem to be fairly close to the reported values of the certified reference materials while higher values are obtained from Dithizone-Chloroform solvent extraction system. However, some results from both of the solvent extraction systems are higher than the reported values. This is because of the contamination during the analysis.

The Improved Solvent Extraction Method may be applied to other metals, Cr, Fe, Cd, or Ag, according to the principle of hard and soft acids and bases. The rule is that acids prefer to bind with hard bases and soft acids prefer soft bases. Thus, the metals, which bind effectively to $(PDC)^-$, soft base, should be the soft acid group(103).

The improved method will remove the salt matrix, which is a source of interference in the analysis by AAS, from the trace metals. From the results of validation with the certified reference materials, which have the various salinities, it also confirms that this technique should be able to be applied with fresh, brackish and sea waters successfully. Therefore, the improved method can be used for the analysis of trace metals in any kinds of natural water samples.

As mentioned earlier, this improved method can be used with the water samples having low concentration of metals (ca. 5 ppb). For the

coastal seawater samples, great care must be taken because the concentration levels of metals in the coastal seawater are higher and some optimum conditions such as the quantity of the chelating ligand must be reconsidered. 5 ml of 2% (w/v) APDC may be insufficient to form complexes with all of the metals in sample leading to the incomplete extraction. By considering the amount of Cu, Ni, Pb and Zn in the three types of certified reference material (Appendix 4), the amount of Cu^{2+} in Riverine water is highest ($3.58 + 0.30 \mu\text{g/l}$). Although the amount of Cu is highest among the three certified reference materials, the quantities of APDC is still sufficient to form complexes with Cu and the other analytes. Since the strength of APDC is varied from manufacturer to manufacturer, therefore, one who use this improved method must know the actual strength of APDC before using it as chelating agent and this can be done by titration of a APDC solution with standard Cd^{+2} solution (104). In overall, the developed method should be able to completely extract metals available in natural samples.

Recommendation.

1. The optimum conditions, which are used in this improved method, are well suited for 100 ml of sample having various salinities.
2. It should be further investigated whether this improved method will effectively extract the other trace metals such as Cr, Fe, Cd, Ag.
3. It should be further investigated that under which conditions either the lossing of analytes in 4N nitric acid onto the container wall by adsorption or the changing of analytes into unmeasurable form by AAS will apply to the decreasing of

concentrations of the analytes during the storage period.