CHAPTER I

INTRODUCTION

Mercury, one of trace elements, is known to have important effects on the physiological processes which occur in all living systems. In addition, mercury contamination of the environment has been also recognized as a significant health problem. Its toxicity was well reviewed by Yamkate(1) and D' Itri (2). In consequence, many laboratories throughout the world are actively engaged in investigating and screening a large variety of samples, collected in the environment, for mercury contamination and toxicity. Recently FAO/WHO (3) has provisionally proposed a maximal permissible level of mercury in food (except fish and shellfish) corresponding to 50 nanogram total mercury per gram fresh weight. The analytical method ultilized for the detemination of mercury in such low concentration must therefore be quantitative and extremely sensitive. It must have very low and constant blank value and completely dependable for mercury analysis as well.

Generally the most common used methods for mercury determination in biological samples are neutron activation analysis, atomic absorption spectrophotometry and substoichiometric isotope dilution (4). Other less frequently used techniques are mass spectrography (5), X-ray

fluorescence (6), and polarography (7).

Of these methods, neutron activation analysis is undoubtedly the most important. The reason is its high sensitivity which enables one to determine as little as 10^{-11} gram of many elements in different materials. Non-destructive neutron activation analysis has been reported for the determination of mercury above 0.1 ppm. level (8, 9, 10). However, both useful isotopes of mercury have low energy gamma emissions, usually necessitating a chemical separation of mercury from the activation matrix.

Most separation methods reported in the literatures involve neither acid dissolution followed by a chemical separation specific for mercury nor combustion technique, coupled with NaI(Tl) countings (11-18). However, although this method is widely used, it still requires highly qualified personnel and rather elaborate and expensive facilities such as neutron source, counting equipments etc. The further disadvantage is that activation analysis only measures the total weight of an element and takes no account of different states of combination.

The most popular and widely used method for traces of mercury determination in biological materials is atomic absorption spectrophotometry. Flame atomic absorption spectrophotometry has been used by many workers (19-29) and the sensitivity of 0.008 ppb. for mercury was obtained. Later Brandenberger (30) found out that there are some disadvantages

of atomizing gas molecule in a flame. Consequently, Brandenberger and Bader (31) and others (32-43) modified and developed the old technique to a flameless atomic absorption spectrophotometry. However, this technique is still having disadvantages such as the instrument is expensive and the technique is more specific.

Substoichiometric isotope dilution is a promising technique for trace elements analysis. The method is quite sensitive and highly selective beside it requires very simple counting devices and less expensive. Its great advantage as compared with other analytical methods lies in that, for the analysis to be successful, it is not necessary to separate quantitatively the component to be determined from the test mixture.

The first step and very important step in mercury determination is to release the mercury from its bonds in sample matrices. Actually, there are only two techniques, i.e. a wet digestion and a dry combustion. However, precaution must be taken in both cases in order to prevent the lpss of mercury by volatilization.

Kimura and Miller (44); and many workers (45-56) developed the wet oxidation procedures to eliminate the loss of mercury. There are, however, some disadvantages of the wet oxidation procedure, that is, time consuming and often tedious operation.

In an attempt to speed up mercury residue analyses and eliminate the loss of mercury by volatilization. Gutenmann and Lisk (57) proposed the technique of burning dried samples in an oxygen-flask with a balloon attached to the side arm for pressure control. Burning of organic materials in an atmosphere of oxygen can be accomplished either in a closed system (57, 58) or in a stream of oxygen (59). Besides, there are several advantages. It is fast, simple and can be performed with a very low blank value. Oxygen can be purified from mercury much more easily than from mineral acids and being commercially available in sufficiently pure form, it is also cheaper than suprapure chemicals. The volatility of mercury is an advantage here because mercury can be quantitatively recovered even from incompletely burned sample (4). Further, when radiomercury is used as a tracer, isotopic equilibrium is rapidly attained in the vapor phase. Pappas and Rosenberg (60-62); white and Lisk (63) used this technique to determine mercury in various sample matrices successfully.

The volume of decomposed samples usually varies between 50 and 100 millilitre of an acid aqueous solution, which also contains different oxidants. Besides that, a number of elements in varying amounts may be present, depending on the nature of the sample. It is therefore necessary to separate and also to preconcentrate mercury before the final determination. This can be done by

distillation, coprecipitation, ion exchange, volatilization, amalgamation or solvent extraction. However, only the last three techniques have found wider application among which solvent extraction has been used most extensively.

In Thailand, at present, the problem of mercury contamination in the environment is well realized. In addition, there is evidence that substantial quantity of mercury compounds are used in Thailand for industrial and agricultural purposes. Although there is no evidence of harmful contamination of mercury in foods, food-products, etc. for the time being, there is the real need for some monitoring. However, the work on mercury contamination has not yet been widely conducted, and a reason for this is probably due to the fact that conventional analytical techniques are not readily applicable for the determination of such element at very low level and the sensitive techniques which described earlier require quite elaborate and expensive equipments. Since substoichiometric isotope dilution is very sensitive and possible to be carried out. In addition, there is not much work has been done in Thailand till present, it is the purpose of the present study to develop the substoichiometric isotope dilution technique for tracesof mercury determination using the combination of dry combustion technique and solvent extraction. The method was primarily tested in radiotracer experiments and then by analysing some already certified

Standard Reference Materials; Orchard Leaves and Bovine Liver of National Bureau of Standards as well as Kale sample of Professor Dr. H.J.M. Bowen of UK. which was distributed by International Atomic Energy Agency (IAEA).