APPENDIXES

APPENDIX A

Analytical methods for lead determination

Numerous methods have been developed for the quantitative determination of lead in environmental and biological samples, namely: atomic absorption spectrophotometry (AAS) [87], optical emission spectroscopy using ICP as excitation source [88], X-ray fluorescence (XRF) [89], isotope dilution mass spectrometry (IDMS) [90], colorimetric or spectrophotometric analysis using dithizone, and electrochemical methods[11] (voltammetry). The majority of these methods is restricted to the measurement of the total lead and cannot directly identify various compounds of lead.

For AAS, lead atoms in the sample must be vaporized either in a precisely controlled flame or in a furnace. Furnace system in AAS applying graphite tubes or cups offer a high sensitivity and the possibility to analyze small samples. AAS is currently the preferred method for routine lead analyses in environmental and biological specimen [87].

Optical emission spectroscopy is based on the measurement of light emitted by elements when they are excited in an appropriate energy medium. The technique has been used to determine the lead content in soils, rocks, minerals, and airborne dusts at 5-10 μg/g level. The primary advantage of the method is that it allows a simultaneous measurement a larger number of elements in small samples. More recent activities have focused attention on the inductively coupled plasma (ICP) system as a valuable means of excitation and analysis [88]. The ICP system offers a high degree of sensitivity with less analytical interference than other typical emission spectroscopy systems.

X-ray fluorescence also allows the simultaneous identification of several elements using a high energy irradiation source. The method is based on the principal that an intense electron beam, which is directed on a sample, produces several forms of radiation,

including X-rays, the wavelengths of which depend on the elements present in the material, and their intensities depend on the relative quantities of these elements. The technique offers the advantage that the sample degradation can be kept to a minimum. It has been used, e.g., for the in vivo determination of lead in teeth and bones [89].

Isotopic dilution mass spectrometry (IDMS) is the most accurate measurement technique presently known. No other technique serves more reliably as a comparative reference technique. IDMS has been used for analysis of subnanogram concentration of lead in a variety of sample types. The isotopic composition of lead produced from ores of different origins has been used as a means of tracing the origin and distribution of anthropogenic lead [90].

Calorimetric analysis of lead using dithizone as the reagent is a "classical" method which has been used for many years. Prior to the development of the IDMS method, it frequently served as a reference method. Differential pulse polarography (DPP) and anodic stripping voltammetry (AVS) offer sufficient analysis sensitivity for most lead measurements in environmental and biological samples. Current practice with commercially available equipment allows lead analysis at subnanogram concentration with a precision of about 5-10% on a routine basis.

APPENDIX B

Applications of adsorptive stripping voltammetry

The possibility of measuring substances by means of adsorptive preconcentration prior to the voltammetric scan has been considered for more than twenty years, but these early reports have been overlooked by analysts. The majority of adsorptive stripping procedures and applications have appeared over the last five years. A variety of important electroactive and nonelectroactive species, possessing surface-active properties, have been determined. The nonelectroactive surfactants have been quantified from the tensammetric (adsorption/desorption) peaks produced during the potential scan. These developments include trace measurements of drugs and other compounds of biological significance, e.g., adriamycin [26], codeine [29], diazepam and nitrazepam [32], phenothiazine tranquilizers [23,25], riboflavin [16], cimetidine [33], monensin [36], heme [24], dopamine [30,31], and deoxyribonucleic acid (DNA) [37], as well as compounds of environmental significance such as thiourea [17] nitro- and triazine-group-containing pesticides [34], and trichlorobiphenyl [35] and other important analytes, e.g., butylated hydroxyanisole [27]. Adsorptive stripping measurements of organic compounds are summarized in Table 1.3. In addition to measurements of organic compounds, the technique has been successfully applied to measurements of metal ions, following the formation and accumulation of surface-active complexes. These studies include trace measurements of nickel [39,40], cobalt [42], uranium [38], vanadium [43], copper [44], lanthanum, praseodymium, cerium [41] and iron in the presence of dimethylglyoxime [39] bipyridine [40], catechol [43,44] pyrocatechol [38] and o-cresol-phthalexon. Extremely low detection limits, e.g., 10^{-10}-10^{-11} M are obtainable for metal ions that cannot be measured conveniently by conventional anodic stripping voltammetry due to low solubility in mercury, irreversible metal/metal ion couple, extremeredox potentials, or formation of intermetallic compounds. Such detectability is comparable to that achievable with modern atomic absorption measurements. Table 1.4 summarizes measurements of metal ions based on adsorptive stripping voltammetry.

Examples of practical applications of these procedures include direct measurements of adriamycin [26], chlorpromazine [23], thiourea [17] and cimetidine [33] in urine, and uric acid in blood samples, methyl-testosterone in pharmaceutical tablets thiourea in cattle feed [17], cobalt in biological samples [40], uranium [38], nickel[39], vanadium[43], iron [95], trichlorobiphenyls [35], pesticides [34] and other surfactants in various natural water samples, butylated hydroxyanisole [27] in food samples, and purity checks. For many practical problems, the selectivity improvement (achieved by the medium exchange procedure) is more significant than that of the sensitivity. As a result, complex samples, such as urine, may be analyzed without any preliminary treatment using a fast and simple procedure.

It has been suggested recently that adsorptive stripping measurements of metal ions can be useful for speciation studies in natural waters. For example, the complexing capacity and conditional stability constants can be determined by means of a stepwise metal titration of the water sample. Unlike conventional anodic stripping voltammetry, no dissociation of natural organic complexes takes place during the accumulation, and the concentrations are determined under true equilibrium conditions. The method was applied for study of copper organic ligands interactions in seawater.

Another unique application relates to the behavior of DNA in biological systems. Valenta and Nurnberg [37] demonstrated that native DNA can be reduced at mercury electrodes after adsorption and unwinding of the double helix. As a result, the adsorption accumulation permits investigations such as binding of antitumor antibiotics with DNA or assessing the damage in native DNA by small γ-radiation doses.

APPENDIX C

Interference in adsorptive stripping voltammetry

The major type of interference in adsorptive stripping measurements is the presence of other surface-active species in the sample solution. These species can affect the accumulation via a competitive coverage. As a result, the stripping peak of interest is depressed or may eventually disappear. For example, 1 ppm of gelatin results in 25% and 45% depressions of the bilirubin and riboflavin, respectively, stripping peaks [16]. The extent of these changes depends on the relative affinities of the analyte and interference towards the surface and their concentration ratio. (Similar interference-with somewhat lesser extent-may be observed in conventional stripping analysis were the surfactant layer blocks the metal deposition.) The presence of halide ions, which exhibit specific adsorption, can result in similar effects. These changes may pose serious problems, especially when biological samples are concerned. Knowledge of these changes is required for minimizing their effects. From the analytical point of view, these interferences can be minimized or eliminated using various approaches. Since the depression of the peak current depends on the fraction of the surface covered by the interfering surfactant (independent of the analyte concentration), calibration curves or standard addition measurements made uniformly-using the sample control-should correct for these effects [26]. Obviously, the linear range is altered by the presence of other surfactants. Surfactant interference can also be alleviated by using shorter accumulation times [32], all with a proper choice of an accumulation potential [17]. This approach are suitable for all models (10-50%) peak depression. More severe peak depressant required preliminary treatment of the sample. Among the proposed treatments suggest for this propose are separation of interfering surfactants by molecular at exclusion chromatography (on Sephadex)[32] or by high performance liquid chromatography [33,35]. Chemical treatment of the sample may also be useful in various situations. Effective correction of surfactant interferences can be achieved when surface-active complexes are used to measure metal ions. In this case, interfering surfactants are

destroyed by UV irradiation prior to adding the complexing ligand of interest. Sample acidification is recommended prior to this treatment to minimize losses of absorption on the walls of the quartz tube used.

Besides its competition on the surface sites, the surfactants may yield a stripping peak (redox or tensammetric) Accordingly, two absorbable species may be measured simultaneously depending upon their peak potentials and relative concentrations (e.g., diazepam and nitrazepam). If both mixture components have similar properties (accumulation and potential) and behave additively, a single peak is obtained, the height of which depends linearly on the total concentration. Mixtures of components which have similar peak potentials, but behave non-additively, require a prior separation step using the chromatographic techniques discussed earlier. Solution-phase (non-adsorbable) electroactive species may interfere depending upon their peak potentials and concentrations. Such interferences can be eliminated using the medium-exchange approach.[22,23] Masking with EDTA can also be useful when these interferences are reducible metal ions [35]. Measurements of metal ions, based on complex formation and adsorption, can be affected by the presence of other metals capable of forming complexes with the complexing ligand. In most cases, a proper choice of the ligand or solution conditions can minimize this type of interference.

As in conventional stripping analysis and other trace methodologies, the reliability and validity of adsorptive stripping data strongly depend upon the degree to which contamination can be minimized. Accordingly, adequate attention should be paid to reduce the contamination risks.

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1. T. Lelasattarathkul, P. Sukkaw, W. Oungpipat and S. Liawrunagrath, "Determination of Yttrium by Flow Injection Spectrophotometry", 26th Congress on Science and Technology of Thailand, Bangkok, 2000.
2. T. Lelasattarathkul, W. Oungpipat and S. Liawrunagrath, " Determination of Yttrium by Flow Injection Spectrophotometry", RGJ Seminar Series II-Analytical Chemistry and Chemistry in the North, Chiang Mai, 2000.

3. T. Lelasattarathkul, W. Oungpipat and S. Liawrunagrath, "Determination of Ascorbic Acid by Flow Injection Analysis Using Thermistor As Detector", 27th Congress on Science and Technology of Thailand, Hatyai, 2001.