# Monitoring of Metal Concentrations in Plating Rinse Tanks Using Stripping Voltammetry

By J. Wang, V. Edwards, J. Lu and H. Tobias

**The utility of electrochemical sensors, based on stripping voltammetry, for monitoring the concentration of toxic metals in electroplating rinse tanks is described. New concepts in stripping voltammetry, based on the use of ultramicro- and modified electrodes and an adsorptive preconcentration step, successfully address many of the requirements for controlling rinsewater composition. The utility of these new sensing devices and strategies are illustrated for measurements of copper, nickel, tin, chromium, cadmium and lead. The high sensitivity of stripping voltammetry, coupled with its compact and low-cost instrumentation, holds great promise for on-site monitoring of trace metals in plating facilities.**

Monitoring and controlling rinsewater composition is important, not only for quality assurance in multi-step processes, but also for minimizing waste. With increasing environmental regulations and waste treatment costs, there is a strong incentive to minimize the volume of rinsewater waste and to be able to document that allowable discharge limits have not been exceeded. There are several ways to reduce the volume of rinsewater while maintaining adequate rinsing, such as using countercurrent rinses, withdrawing the parts slowly from the process tank, allowing adequate time for drainage, racking the parts intelligently, etc., but any method for minimizing the rinse waste volume requires a means for monitoring the cleanliness of the water to ensure that both process and regulatory requirements are met. The methods currently in use for controlling rinsewater cleanliness range in sophistication from no control at all to timers to conductivity-controlled valves. Except for the case of no control, each represents an improvement because more information is available to optimize the rinsing and to document the effluents. The next step beyond conductivity control is chemical monitoring and control. The potential advantages of chemical monitoring over conductivity measurements include the ability to provide the needed monitoring for waste treatment, recovery and recycle, and to document effluent species and concentrations.

At present, chemical monitoring is not generally considered feasible for use on the shop floor because of high cost, slow response time (especially if an outside laboratory is required), size, maintenance requirements, etc. Monitoring methods currently used include titration, atomic absorption spectroscopy (AA), and inductively coupled plasma-atomic emission spectroscopy (ICP-AES). These require either sending the samples to an outside laboratory, which is costly and time-consuming, or providing trained personnel and laboratory space at the plating facility.

Simple, inexpensive electrochemical sensors are available that could be used off-line on the shop floor, with automated sample and chemicals handling, to monitor, in the ppm and sub-ppm range, a variety of ions, such as copper, lead, tin, cadmium, chromium and nickel. Electrochemical devices have achieved wide acceptance for chemical sensing, and have proven themselves for clinical monitoring[1,2] and environmental surveillance.[1,3,4] While such applications have relied on the use of ion-selective electrodes, amperometric enzyme electrodes, or membrane-based, gas-sensing devices, the current work is based on adaptation of stripping voltammetry for on-site monitoring of trace metals in plating facilities.

Stripping voltammetry consists of accumulating a species onto an electrode, then stripping the species off electrochemically and measuring the stripping current vs. applied voltage. The species, such as lead, cadmium, etc., can be accumulated by plating it onto a bare electrode, such as carbon or platinum, or by amalgamating it with mercury. In either case, the plating is done at a constant voltage at the mass-transfer limiting current. The advantage of the amalgamation method is that the mercury suppresses the hydrogen evolution reaction that competes with the desired accumulation reaction. The mercury can be either preplated as a very thin film onto an electrode, making a so-called "mercury film electrode," or it can be added in ionic form to a grab-sample and be codeposited with the species of interest. The major disadvantage of the amalgamation method is the need to dispose of or recycle the hazardous mercury. For this reason, we have tried to show the feasibility of reusable preplated mercury film electrodes. The amalgamation reaction is shown in the "preconcentration" portion of Fig. 1A.

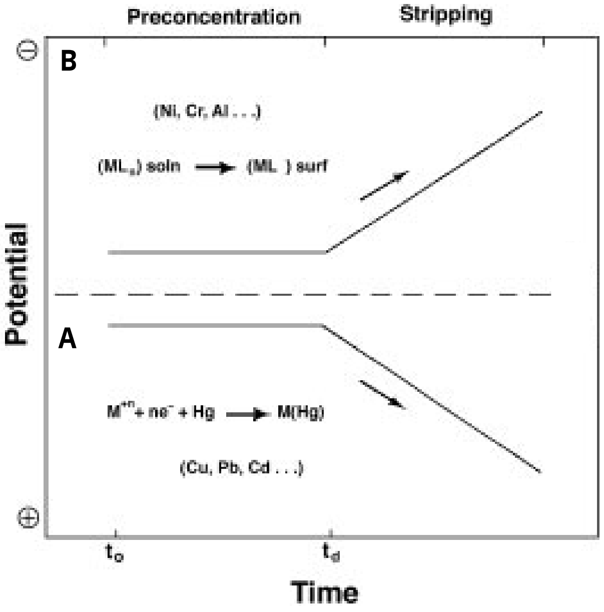

*Fig. 1—Schematic: Preconcentration-stripping cycles employed in conventional (electrolytic) (A) and adsorptive (B) stripping schemes.*

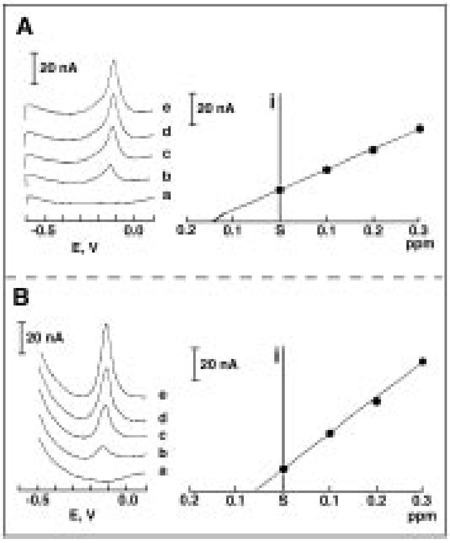

*Fig. 2—Determination of copper in copper rinse samples. Voltammograms for tap water (a), sample spikes (4 x $10^4$ dilution) (b) and subsequent concentration increments of 0.1 ppm copper (c-e). Mercury-coated carbon fiber electrode, with 2 secpreconcentration at -0.60 V and a differential pulse waveform. Unstirred solutions containing dissolved oxygen. (A) Acid copper (B) Electroless copper.*

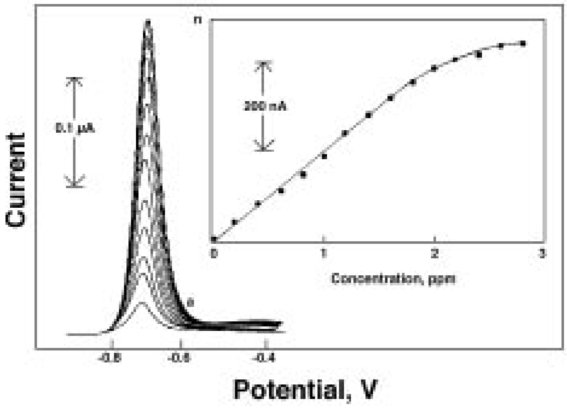

*Fig. 3—Stripping voltammograms obtained at the mercury-coated carbon fiber electrode for cadmium solutions of increasing concentration in 0.2 ppm steps (a-n). Also shown is the resulting calibration plot. Preconcentration at -1.2 V for 2 sec, coupled with a differential pulse waveform. Medium—unstirred tap water containing dissolved oxygen.*

Another method for accumulating the species, that requires no mercury, is to use a chemical ligand to complex the species and allow it to be adsorbed onto the electrode. This adsorptive accumulation scheme is shown in Fig. 1B. The stripping step consists of sweeping the potential in the proper direction to dissolve or desorb the species from the electrode, as shown in the "stripping" portion of Fig. 1. When the potential reaches the redox potential of the accumulated species, the current will rise until the species is depleted from the electrode, at which time the current will fall. Consequently, a current peak will result; the height of the peak is proportional to the amount of species accumulated, and the potential at which it occurs is determined by the identity of the species.

Stripping voltammetry couples the advantages of excellent sensitivity (with sub-ppb detection limits), speed and accuracy, with compact/inexpensive instrumentation and low power demands.[1] The remarkable sensitivity of the overall method is attributed to the coupling of an effective in-situ preconcentration step with an advanced measurement scheme. About 30 metals can thus be determined; the operation is fast (1-3 min/assay), precise, simple and suitable for automation.

Recent advances in stripping voltammetry, particularly the development of new adsorptive stripping procedures,[4] and the introduction of micro- and modified stripping electrodes,[5] have greatly enhanced sensing capability. Such new sensing capabilities are illustrated in the following sections in connection with chemical characterization of rinsewater.

## Equipment and Procedures

Experiments were performed with a voltammetric analyzer.[a] The working electrodes included a mercury-coated carbon fiber cylinder (8 µm dia., 2 mm length), a static mercury drop electrode[b] or a dimethylglyoxime-modified carbon paste electrode. Platinum wire and silver-silver chloride served as counter and reference electrodes, respectively. Experiments were carried out in a 10-mL electrochemical cell, placed on a magnetic stirrer. The preconcentration period (over a selected time) was followed by a differential pulse measurement of the accumulated species.[1] Plating solutions received from AlliedSignal Aerospace Co. (Kansas City Div.), were diluted with tap water to simulate rinsewater.

## Results and Discussion

Stripping voltammetric sensors, based on ultramicroelectrodes, are particularly useful for monitoring metal concentrations in plating rinse tanks. Such microelectrodes offer many attractive features over conventional-sized electrodes, including reduced ohmic resistance effects and high rates of mass transport.[6] Accordingly, it is possible to assay rinse tank samples without deliberately adding supporting electrolyte or stirring the solution during the deposition.

Figure 2 shows the standard addition stripping voltammograms taken in copper plating solutions diluted 40,000-fold with tap water to simulate clean rinse water (A—acid copper, B—electroless copper). The standard addition technique is to add known increments of copper to the unknown sample and extrapolate the linear plot of peak current vs. concentration to determine the unknown sample concentration. Curve a is the tap water, b is the simulated rinsewater sample, and curves c–e are the sample, spiked with 0.1 ppm increments of copper.

The data in Fig. 2 were taken without stirring, removing oxygen, or adding supporting electrolyte to assess the feasibility of using these sensors directly in the rinse tank. Direct use requires insensitivity to stirring (because the velocity of solution flowing past the sensor would be variable and unknown), insensitivity to dissolved oxygen, and the ability to function without any added chemicals, such as a buffering agent.

A large, conventional (macro) glassy-carbon Hg-coated electrode would be completely unsuitable for this application because a trial stirring with a magnetic stirrer caused a 9-fold enhancement of the copper stripping peak (data not shown). The particular sensor used, the 8 µm x 2 mm carbon fiber, is superior to the macroelectrode, but is still too sensitive to stirring, because the copper stripping peak was enhanced by a factor of 1.8. Further minimization of stirring effects, needed for in-situ applications in rinse tanks, would require the use of even smaller ultramicroelectrode arrays.

The presence of dissolved oxygen presents no obstacle to stripping analysis, as shown by the sharp peaks in Fig. 2 for air-saturated solutions. Even better accuracy can be attained

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[a] Model 264A, EG&G PAR, Princeton, NJ.

[b] Model 303A, EG&G PAR, Princeton, NJ.

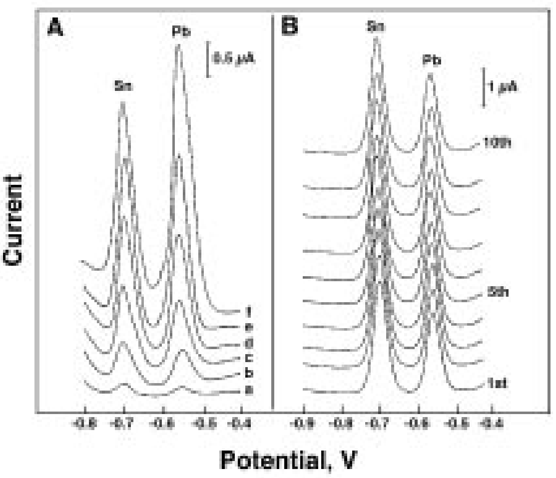

*Fig. 4—Stripping voltammograms for mixtures of tin and lead obtained at the mercury-coated carbon fiber electrode. (A) voltammograms for 10 ppb lead and 50 ppb tin following different preconcentration times: (a) 0, (b) 30, (c) 60, (d) 120, (e) 180 and (f) 240 sec. (B) Repetitive measurements of 20 ppb lead and 50 ppb tin, following 60 sec deposition. Differential pulse waveform with 25 mV amplitude and 5 (A) and 10 (B) mV/sec scan rate. Electrolyte: 0.2 M citric acid (pH 3.9).*

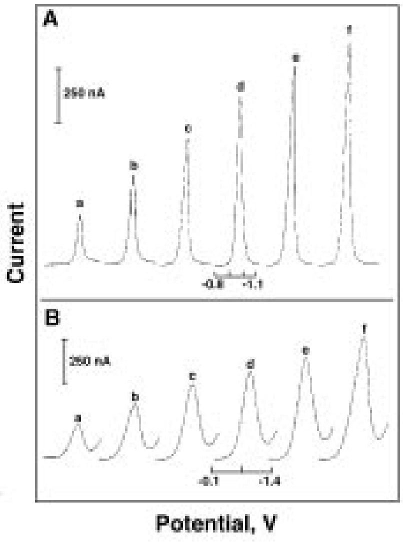

*Fig. 5—Adsorptive stripping voltammograms for (A) nickel and (B) chromium(VI) solutions of increasing concentration in 5 ppb steps from 5 to 30 ppb (a-f). Preconcentration for 20 sec at (A) -0.40 and (B) -0.80 V. Solutions, (A) tap water containing 1 x $10^{-4}$ M dimethylglyoxime; (B) tap water containing $10^{-2}$ M diethylenetriamine pentaacetic acid (DTPA) and 5 x $10^{-2}$ M sodium nitrate. Hanging mercury drop electrode and differential pulse waveform.*

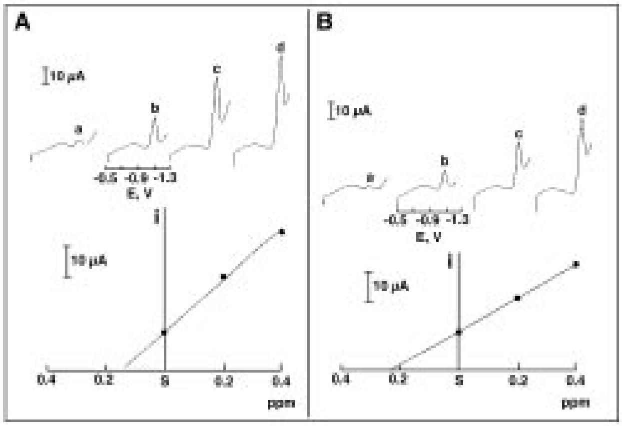

*Fig. 6—Determination of nickel in nickel plating solutions diluted with ammonia buffer: (A) electroless Ni diluted 40,000:1; (B) Woods Ni diluted 400,000:1. Voltammograms for (a) ammonia buffer blank; (b) sample spikes; and (c, d) subsequent concentration increments of 0.2 ppm nickel. Carbon-paste electrode modified with dimethylglyoxime, with 60 sec preconcentration, differential pulse waveform, and 30 sec cleaning in nitric acid to restore the electrode between measurements.*

by performing a background subtraction to eliminate the effect of oxygen.[1]

The main obstacle to using these sensors directly in a tank is the need to add chemicals. Although separate calibration curves could be obtained for each type of copper plating solution [note that the slopes of the curves A (acid copper) and B (electroless) are different], the standard addition method is expected to give better accuracy because it eliminates matrix effects.

The reproducibility of these measurements is strongly dependent on the mercury electrode preparation procedure. For the carbon-based mercury-film electrodes used here, 15 repetitive measurements of the stripping peak for the simulated acid-copper rinse sample gave a relative standard deviation of 2.3 percent. In fact, the microelectrode exhibited high stability over an entire day of operation.

Measurements of cadmium, which is also of major concern to the plating industry, can also be carried out by stripping-based microelectrodes. Figure 3 displays typical calibration data for cadmium, in tap water, over the 0-2.8 ppm range, using the mercury-coated carbon fiber. Well-defined peaks are observed for these 0.2 ppm concentration increments, following a 2-sec deposition. Linearity prevailed up to 2.0 ppm, with a leveling off at higher concentrations because of saturation of the mercury film. Analogous measurements at the bare carbon fiber suffered from a limited linear range (up to 0.5 ppm).

The mercury-coated carbon fiber electrode can also be used for the simultaneous measurement of lead and tin. Figure 4a illustrates voltammograms for a mixture of 50 ppb tin and 10 ppb lead, following different preconcentration times (0–240 sec, curves a–f). Both metals yield well-defined and resolved peaks that increase rapidly upon extension of the preconcentration period. Also shown in Fig. 4b are voltammograms for repetitive measurements of 20 ppb lead and 50 ppb tin. These 10 runs are part of a prolonged series of 20 measurements that yielded a reproducible response (relative standard deviation of 5.2 percent for tin and 4.0 percent for lead).

Adsorptive stripping voltammetry, based on the formation and adsorptive accumulation of an appropriate complex of the metal of interest (Fig. 1b), represents a major advance in stripping analysis.[4] This scheme has greatly expanded the scope of stripping voltammetry toward numerous metals that cannot be accumulated by electrolysis. For example, Fig. 5 displays voltammograms for nickel (A) and chromium (B) solutions of increasing concentration (5–30 ppb, a–f), following a 20-sec preconcentration in solution containing added ligand. Convenient quantification of these ppb concentrations is indicated from the well-defined peaks for both metals.

Instead of adding the ligand into the sample, as was done in Fig. 5, it is possible to develop a reagent-less sensor, based on incorporation of the ligand onto the electrode surface.[7] For example, Fig. 6 demonstrates the voltammetric measurement of nickel in nickel rinse samples, using a dimethylglyoxime-modified carbon paste electrode. The electrode was modified in accordance with the method of Baldwin and coworkers.[8] The binding (complexing) properties of the modified electrode surface allow effective non-electrolytic preconcentration. The resulting high sensitivity permits convenient assays of the plating baths diluted with tap water (by a factor of 104–105). In addition, high selectivity accrues from the specific coordination reaction.

## Conclusions

It is clear that the power of stripping voltammetry can benefit plating facilities in many practical situations. The recent introduction of adsorptive accumulation schemes, and of new ultramicro- and modified electrodes has greatly enhanced the capabilities of stripping voltammetry for monitoring toxic metals in electroplating rinse tanks. The remarkable sensitivity of this electrochemical method, coupled with its small and inexpensive instrumentation, should greatly facilitate the on-site chemical characterization of rinsewater. Other plating processes could also benefit from the sensitivity, speed, accuracy and portability of modern stripping-based sensing devices.

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