THE USE OF RECYCLED STATIC MERCURY DROP ELECTRODE FOR ELECTROANALYSIS OF HEAVY METALS IN INDUSTRIAL WASTES

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ABSTRACT

The determination of heavy metals in industrial wastewater is carried out with an automated polarographic analyzer. The system is equipped with a recycled mercury electrode, which reduces mercury consumption to a negligible amount. Operation of the system is demonstrated by analyzing a mixture of four metal ions in the $1 mgL^{-1}$ concentration range. During continuous operation over a period of two months the system performed smoothly monitoring ca 10^5 samples. The detection limit for cadmium ions is of the order of ~ $50\ \mu gL^{-1}$. Detailed descriptions of both the system and the electrode are given.

INTRODUCTION

Automated polarographic analyzers are well suited for industrial wastewater analysis, required for monitoring the low concentration levels of heavy metals allowed by environmental agencies. Relatively inexpensive yet effective polarographic methods have been largely supplemented by costlier spectroscopic methods (AAS, ICP) due to environmental concerns related to the risk of possible mercury spills. In principle, this risk should be manageable by reducing the consumption of mercury which, in turn, affects the amounts required for refilling the system and the frequency of the refilling step (during which the risk of mercury spills occurs).

Commercial polarographic analyzers on the average consume ~ 100 grams of mercury per month. Although it seems that this amount is small and the reservoir can be designed to hold a six month's supply of mercury, the main problem of refilling remains. In addition, off-the-shelf commercial electrodes are refilled after either removing the electrode from the polarographic stand, or lifting the lid off the mercury reservoir. In spite of this drawback, many automated flow systems for voltammetric analysis have been proposed; some of them are based on commercial cells and electrodes like the EG&G PARC Model 420 flow cell and the PARC 303 SMDE /1,2/, or the Metrohm HMDE 663 VA Stand /3,4/. Others employ home-made flow cells and electrodes; the flow cells used for monitoring extremely low concentrations of cobalt in natural waters /5/, chromium(VI) in natural water sample /6/ and the cell equipped with a thin-film deaerator and auto-drop driven SMDE /7/ are typical examples.

These cells can hardly be adapted for the routine monitoring of industrial wastes. Some manufacturers offer unattended monitors for heavy metals in water, based on the well known potentiometric or anodic stripping analysis carried out with a mercury film based glassy carbon electrode /8/. Analyte concentrations of the order of 10 ngL^{-1} can be determined /9/. To secure the quality of the film, mercuric nitrate is added to the analyte solution so that mercury is continuously co-deposited with the analyte. While removing the risk of mercury metal spills, significant amounts of mercury ions (up to 40 mgL^{-1}) are introduced and find their way into the outflow of the analytical system.

The continuous use of solid electrodes (e.g., Pt, Au and GC) is limited by the pronounced surface deterioration occurring in real sample analyzers; this is eliminated by covering the electrode with a membrane. Successful instances of this approach include the well established Clark electrode /10/, in which both the protecting membrane and the measurement of current at constant potential contribute to stability. Stability has also been claimed in the case of a more sophisticated, multi-layer electrode for monitoring glucose in blood /11/. Disposable solid electrodes have also been fairly successful, mainly in pocket-size glucose and lead analyzers /12/. These are, essentially, batch analyzers; voltammetric analyzers coupled with solid electrodes require frequent maintenance and are, thus, unsuitable for continuous use in industrial waste waters.

A system which retains the advantages of the mercury drop electrode, with its continuously renewable surface providing excellent accuracy, stability and reproducibility and yet eliminates the risk of mercury spills during the refill step is thus the preferred cost-effective approach to trace metal determination in waste waters. The recycled mercury electrode described below is a proposed solution.

THE DEVELOPMENT OF RECYCLED MERCURY ELECTRODES

The mercury metal, accumulating at the bottom of the polarographic cell, is usually collected and transferred to a large bottle. Untreated mercury is contaminated by amalgam forming metals deposited during the analysis, and thus unusable. Some users replace this spent, contaminated mercury with a fresh supply and ship the former to a hazardous waste disposal site. Others proceed with the cumbersome procedure of chemical treatment followed by distillation. Alternatively, the amalgamated metals may be stripped from the mercury by applying a positive potential to a mecury pool. This procedure requires the transfer of the accumulated mercury waste to a special container equipped with a platinum wire (which forms the electric contact with the mercury) and counter and reference electrodes. An electrolyte solution is propelled into the container at a constant flow rate. The electrodes are connected to a potentiostat; the applied potential should equal the mixed potential of two systems: the most positive redox potential of the amalgam forming metals and the potential at which mercury itself is oxidized. The electrolyte solution serves as a sink for the metal ions stripped from the amalgam and must be collected in a container. Stripping efficiency can be increased by stirring the surface of the mercury pool, but is nevertheless a lengthy process.

The specifications of "clean mercury" depend on the concentration of the metal ions in the analyte; for monitoring concentrations in the 10^{-9} - 10^{-10} molar range, extreme care must be taken to use metal free mercury. For industrial wastes, the concentration range of interest is of the order of 10^{-5} - 10^{-6} M. The use of recycled mercury, as described below, is essentially not time limited only (a very small amount of mercury is consumed by oxidation). Chemical oxidants such as dissolved oxygen may also be used to effect stripping. Oxygen is reduced to hydrogen peroxide at potentials more negative than ~ 0.1 volts vs SCE. As a result, the mercury pool acquires a rest potential at which some oxygen is reduced at the rate of the metal oxidation (including mercury). These simultaneous processes do not require the use of external electrodes and potentiostat. After this corrosion clean-up, the cleansed mercury is returned, by means of a peristaltic pump, to the mercury electrode proper. Any kind of mercury electrode may be used, provided it has an inlet open to the pump tubing. The pump delivers the mercury to the capillary. Two modes of operation are possible: (a) continuous operation of the pump results in a dropping mercury electrode; (b) static mercury drops are formed when pump operation is stopped at a predetermined time after drop fall. The latter is more suitable for square wave voltammetry. These options have led to the development of the final version of the Recycled Static Mercury Drop Electrode (RSMDE).

EXPERIMENTAL

Apparatus

The cell system (Figure 1) consists of three main parts: (a) the deaerator and a peristaltic pump, (b) the polarographic cell proper with working, reference and counter electrodes and a solution outlet connected to a waste bottle, (c) the working electrode system, consisting of a mercury reservoir (~ 5 mL), a peristaltic pump and a tapered capillary (~ 0.5 mm ID, 0.1 mm ID at the tip). The mercury surface in the reservoir is covered with an aqueous solution (e.g., tap water).

The polarographic analyzer and the peristaltic pumps were designed and constructed in the Technical Services of the Department of Chemistry of the Technion. The stepping motors had a torque of 56 onze inch. The operation of the electrode was controlled by an electronic counter. The glassware was made in the glass shop of the Department of Chemistry. Voltammograms were recorded with a Yokogawa model 3027 recorder. The polarographic cell was equipped with a thin-film deaerator /13/ which consists of a glass tube (I.D. ~ 1mm) with two inlets connected to a nitrogen tank (pressure reduced to 0.1 bar) and the outlet of the solution peristaltic pump, and one outlet connected to the polarographic cell. The solution forms a thin layer on the inside wall of the tube (~ 50 μm), resulting in a complete removal of dissolved oxygen (by diffusion to the gas phase).

Reagents

Solutions were prepared from reagent grade KCl, $CdCl_2$, $CuSO_4$, $Pb(NO_3)_2$, $Zn(NO_3)_2$ and triply distilled water. Tap water was added to the mercury reservoir.

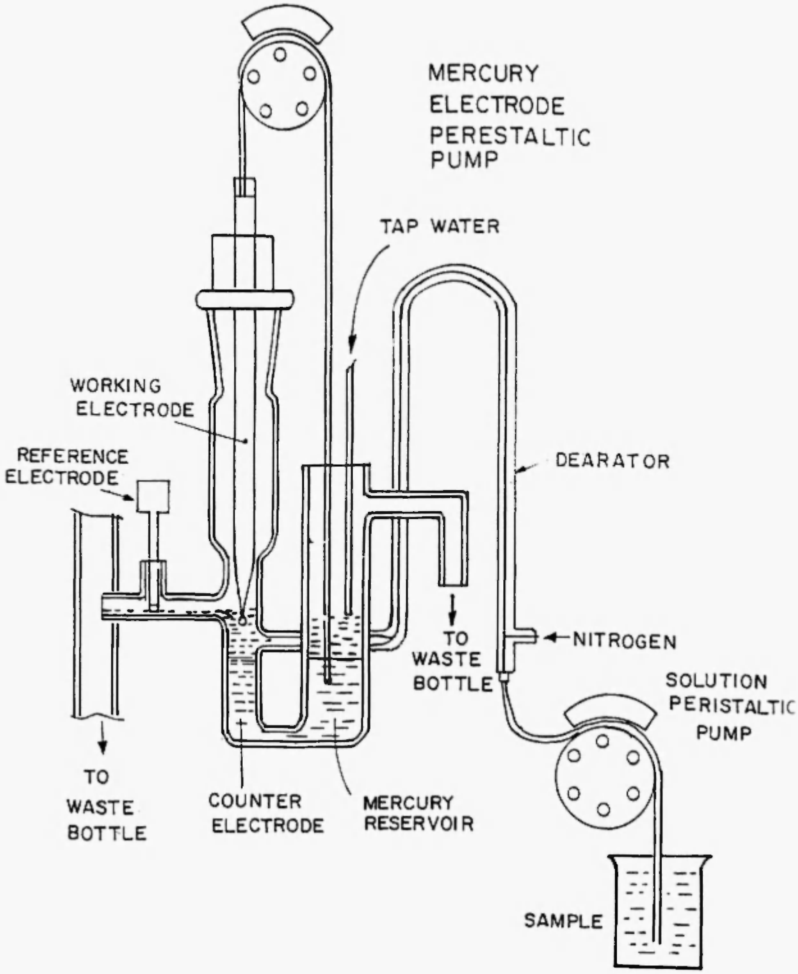

Fig. 1. Schematic diagram of the polarographic cell and the RMSE.

RESULTS AND DISCUSSION

Electrode operation

The cell was connected to the polarographic analyzer and operated in the usual manner: the static drop was dislodged by means of a small knocker, the mercury pump was activated for a short time to produce a small mercury drop and finally the potential scan (with superimposed square wave) was applied and the current monitored. Irreproducible results (± 20%) were attributed to an erratic mercury drop size caused by the flow rate pulses encountered with peristaltic pumps, which could be easily detected with a magnifier. Synchronization of the knocker with the position of the rollers improved reproducibility (± 2%). Creeping of the solution between the inner wall of the capillary and the mercury, leading to deterioration of the base line, and quite often to electrical cutoff, also occurred. To cope with this problem, the knocker and the synchronization device were replaced by the following system: (i) a new peristaltic pump (5 roller head), propelled by a stepper motor advancing 1.8° per step (200 steps per revolution; the motor is advanced one step every four clock pulses), (ii) a drop fall detector, (iii) various electronic devices (controller, pulse generator, counter and power driver) required to control the sequence of events described below (Figure 2): (a) A start command activates the power driver of the peristaltic pump and resets the electronic counter, (b) the drop size increases until the drop is detached from the capillary; the drop fall is detected by measuring the square wave charging current (at the drop fall this current decays, virtually, to zero), and the detection pulse activates the electronic counter connected to the clock input of the power driver, (c) the operation of the pump is stopped on

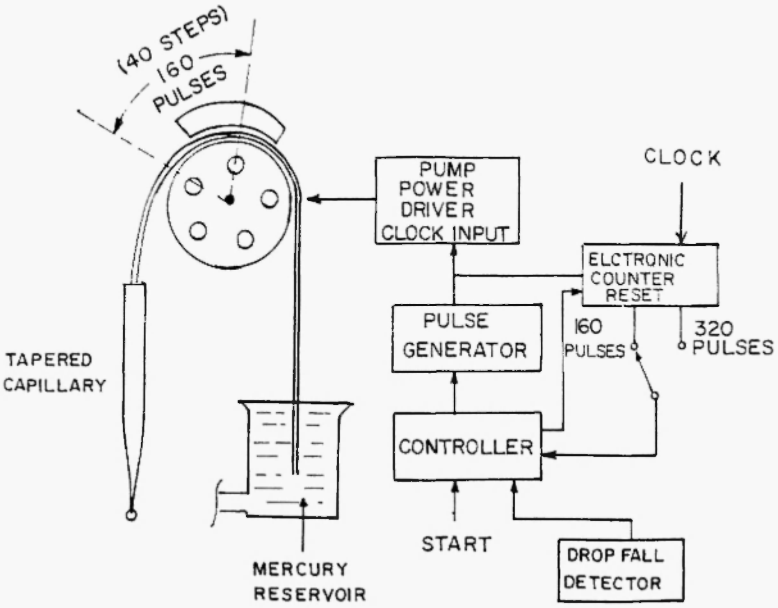

Fig. 2. A block diagram of the electronic driver of the RMSE.

reaching a 160 or 320 count (final drop size is "small" or "large", respectively). The operation is based on the assumption that integration of the flow rate with time (volume) should yield a constant value if the initial and final integration points are matched with the rotation of the pump head (number of pulses per revolution divided by the number of rollers).

This system is less affected by to mechanical problems such as knocker adjustment and creeping of the solution into the capillary.

Short term analysis

The inlet of the tubing of the solution pump was immersed in the analyte solution (mixture of Cu(II), Pb(II), Cd(II), Zn(II) ions in 0.1 M KCl) and the sample was pumped into the cell for 15 s. A "start" command was then applied to the electrode, a fresh drop was formed, and a voltammogram recorded. The "start" command was repeated two more times (in the same solution) to allow evaluation of reproducibility and signal averaging. Some carry-over effects could be seen when the solution containing the above mentioned metal ions was replaced with a supporting electrolyte solution. This effect can be considerably reduced by flushing the cell with the supporting electrolyte solution (or with a new sample) for longer periods of time. Figure 3 compares two typical voltammograms recorded with the RSMDE and the Automatic Voltammetric Electrode /14/. The latter incorporates a simple dropping mercury electrode. The observed different ratio between peak heights stems from the increase of the DME drop with time.

Long term monitoring

The sample tubing inlet was immersed in a four-quart sample container. The sample pump was operated continuously for seven days, at a rate of 120 samples per hour, without recording each successive scan. At the end of each day, a single polarogram was recorded, operation was halted and at the end of the week the seven voltammograms compared. During long term monitoring adsorption effects occur; the plastic tubing is exposed for many hours to high concentrations (1 mgL^{-1}) of metal ions. Figure 4 demonstrates this adsorption effect. A typical voltammogram (4a) recorded after 25,000 cycles reveals some differences in peak currents (as compared to the peak currents shown in Figure 3). The differences are attributed to temperature and flow rate

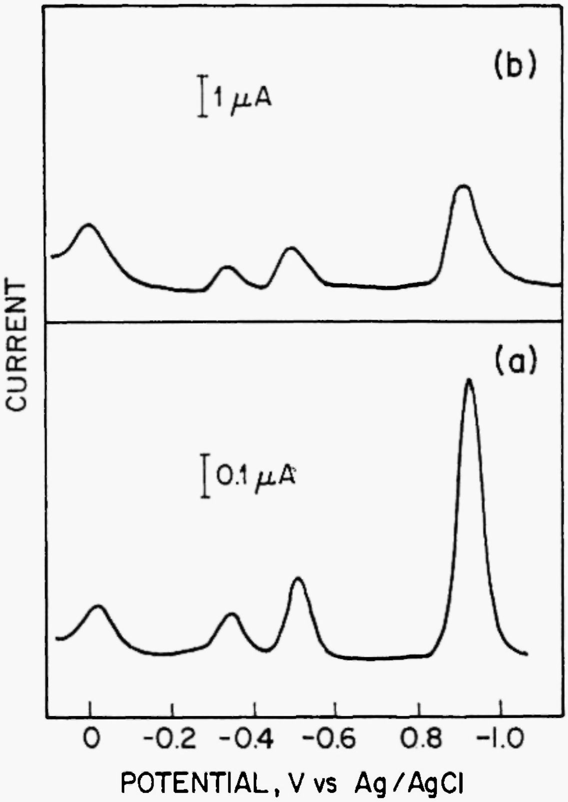

Fig. 3. Square wave voltammogram recorded in a solution containing 1 mgL^{-1} of Cu(II), Pb(II), Cd(II) and Zn(II) with the AVE (a) and with the RMSE (b). Square wave amplitude: 50 mV p-p. Frequency: 25 Hz.

changes. These experiments were further carried out for one month yielding the same peak currents. The adsorption effect is demonstrated by passing pure supporting electrolyte solution through the cell. The voltammogram (4b) reveals peak currents of copper, lead, and zinc, but no peak current of cadmium is observed. In the case of carry over, the peaks of voltammograms reflect analyte composition; adsorption is individual and thus non-adsorbing ions will not be present in the flushing solution. Intermetallic compounds interference, encountered with mercury film electrodes, is minimized by reducing the concentrations of the metals in the mercuric phase /15/; the use of mercury drops eliminates the problem. Indeed, no interferences have been detected in this study.

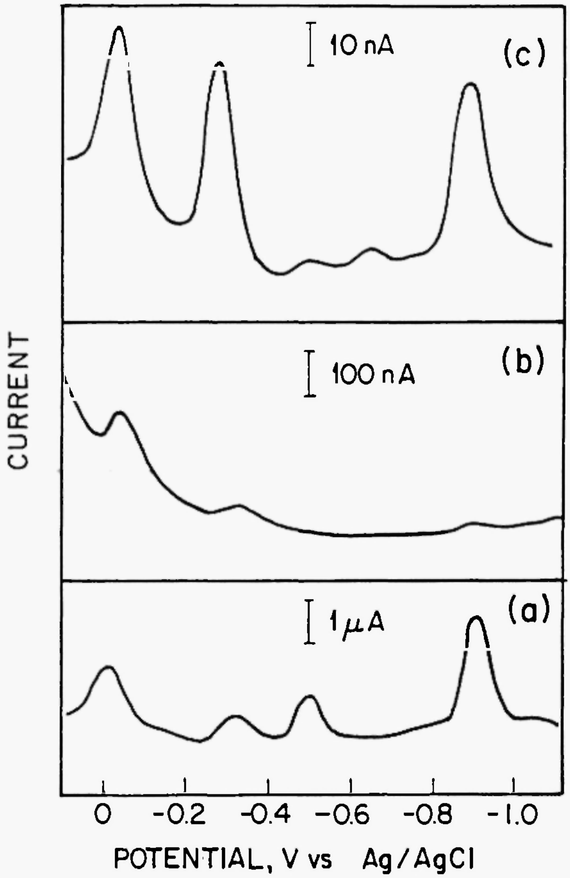

Fig. 4. Square wave voltammograms recorded with the RMSE: the mercury has been recycled for 5 days: (a) Same conditions as in Figure 3(a). (b) Recorded in supporting electrolyte solution. (c) Voltammograms recorded with the AVE in a solution collected after passing the deaerator of the RMSE.

In a preferred approach to the detection of metal ions adsorbed during long term monitoring inside the plastic tubing, the tubing outlet is detached from the deaerator and connected to the AVE and pure supporting electrolyte passed through the tubing. The voltammogram (Figure 4C) shows high concentrations of copper, lead and zinc ions, stripped from the plastic tubing of the sampling pump. The adsorption effect can be appreciably diminished, by replacing the tubing with less adsorbing tubing (like Pharmed), or replacing the pump with a PTFE based metering pump.

Analysis of the recycled mercury

To monitor the quality of the recycled mercury, some was used to fill the reservoir of the SMDE and immersed in a solution of pure supporting electrolyte and a square wave voltammogram recorded. This procedure was necessary to detect residual traces of heavy metals present as amalgams. The mercury was returned to the reservoir of the RMSE after analysis. "Clean" mercury should reveal no peak currents. Voltammograms indicate that the concentration of metals in the mercury to be of the order of 2-5 μgL^{-1} as Cd. This level remained unchanged throughout a period of two months. In practice, the system is applicable to industrial waste solutions with metal ion concentrations exceeding 20-50 mgL^{-1}.

Analysis of the clean-up solution

The clean-up solution was also tested with the AVE. The flow of tap water was stopped after the solution covering the mercury pool (~10 mL) had been used for a long time (1 week)) and a stream of air had been passed through the solution by means of a small bubbler connected to an air pump (1.2 L min^{-1}). As the result of the corrosion process occurring at the surface of the mercury pool, some amounts of mercury were detected (~10 mg). The corrosion rate of mercury may be assumed to be constant throughout this process, a flow of tap water at a rate as low as 10 L per week is, therefore, sufficient to reduce the concentration of mercury ions in the waste solution to 10 μgL^{-1}.

CONCLUSIONS

The recycled mercury electrode offers a new approach to unattended, automated polarographic analyzers which consume negligible amounts of mercury and, therefore, can be used for a very long time without resorting to the mercury reservoir refilling step. The monitored solution must be introduced by an appropriate pump (e.g., PTEE based metering pump) to avoid adsorption of metal ions.

FUTURE DEVELOPMENT

Real samples contain some organic components and contaminants, which can adsorb on the mercury electrode, and interfere with the electrodic reaction, causing the attenuation of faradaic currents. A state-of-the-art analyzer for metal ions in industrial waste water should include a device for sample pre-treatment (digestion-ultrasonic or microwave) and an electrochemical analyzer. Such a system is now under construction; its evaluation will be presented in the near future.

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