



Microfabricated electrochemical analysis system for heavy metal detection

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Abstract

A low power, hand-held system has been developed for the measurement of heavy metal ions in aqueous solutions. The system consists of an electrode array sensor, a high performance single chip potentiostat and a microcontroller circuit. The sensor is a microfabricated array of iridium electrodes, onto which a thin film of mercury is electroplated. Quantitative heavy metal analysis is performed using square-wave anodic stripping voltammetry. Measured results show a one part-per-billion sensitivity and multiple use capability.

Keywords: Heavy metal; Potentiostat; Square wave anodic stripping voltammetry; Microelectrode

1. Introduction

There is an increasing need for in situ analysis of heavy metal contaminants in drinking, industrial and ground water samples. Toxic metals such as lead, cadmium and arsenic enter water supplies through landfills and plumbing, and are health risks even in trace quantities. In integrated circuit fabrication, heavy metal surface contamination can have a significant detrimental effect on threshold voltage and gate oxide reliability.

Traditionally, water samples are collected and physically transported to central laboratories for analysis. In a number of applications the long time delays associated with this procedure are unacceptable, and on-line monitoring may be required. In addition, the majority of samples are typically negative, yet are subjected to costly laboratory analysis. A field-portable instrument for threshold detection could save resources by employing costly analysis only on positive samples. Most modern heavy metal analysis systems are too expensive, power-inefficient and bulky for field work. In order to improve on this, an inexpensive portable electrochemical analysis system was developed.

2. System description

The core of the analysis system is a microfabricated electrochemical sensor and a high-performance single-chip potentiostat. These components are combined with a microcontroller to create a complete miniaturized computer-controlled chemical analyzer (Fig. 1). The chemical sensor is a chip containing a mercury-on-iridium working electrode array (where the chemical reactions of interest occur), a Ag/AgCl reference electrode and an iridium counter electrode. The potentiostat is a CMOS chip that controls the potential between the working and reference electrodes at a value set using an on-chip D/A converter. A dual-slope, current input A/D converter holds the working electrode at a virtual ground and digitizes the electrode current. The microcontroller orchestrates the analysis by setting the DAC values and recording the ADC results. The system is battery powered and only 1 × 3 × 5 inches in size. A communications link is used to transmit data to the parallel port of a laptop computer for plotting and data analysis. This analysis system can measure many heavy metal ion species in unmodified water samples with one part-per-billion sensitivity.

3. Heavy metal analysis

The chemical analysis is performed using square-wave

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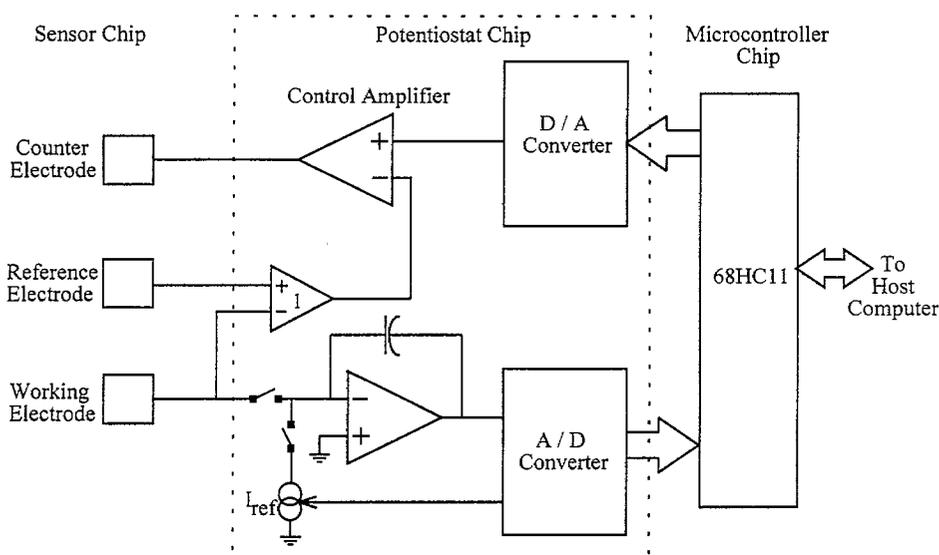


Fig. 1. Schematic of the heavy metal analysis system. The three electrodes are located on a sensor chip, the analog electronics and data converters are on a single CMOS chip, and a 68HC11 microcontroller is used to control the analysis and record the results.

anodic stripping voltammetry (SWASV) [1,2]. The SWASV technique uses a mercury electrode placed into the solution to be analyzed. The electrode is first held at a cathodic potential so that metal ions from the solution are reduced at the surface of the mercury and dissolved within it. This serves as a 'preconcentration' step to greatly increase their concentration within the mercury (Fig. 2a).

After the preconcentration step, the voltage applied to the electrode is scanned in the anodic direction to reoxidize the metals dissolved in the mercury. As the voltage reaches the redox potential of a given species, that metal will reoxidize. This causes a peak in the electrode current which is proportional in amplitude to the metal ion concentration in the solution. If multiple metal species are present, several current peaks will be seen as the potential is swept anodically (Fig. 2b).

During the stripping stage, a square wave is superimposed on the linearly ramped voltage applied to the electrode. The difference between the currents at the end of each phase of the square wave is plotted versus the ap-

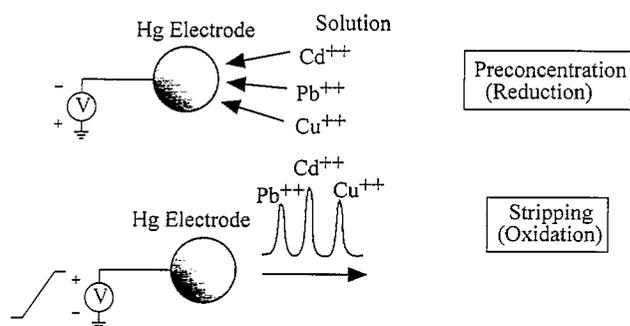


Fig. 2. Conceptual diagram illustrating anodic stripping voltammetry in the preconcentration and stripping stages of the analysis.

plied electrode potential to obtain a voltammogram showing peaks corresponding to different heavy metals. This differential current measurement technique cancels error currents due to capacitive charging and improves the dynamic range of the analysis.

4. Mercury microelectrode array

The electrochemical sensor is an improved version of the sensor described in [3]. It consists of an array of electrically connected, diffusively isolated iridium microelectrodes fabricated by a lithographic lift-off technique. A passivation layer of silicon nitride covers the structure and is etched away in regions where the microelectrodes are to be exposed (Fig. 3). The fabrication process is described in [3].

After fabrication of the iridium electrodes, mercury hemispheres are electroplated onto the exposed iridium, creating miniature static mercury drop electrodes. The mercury hemispheres are physically stable and strongly adhere to the underlying electrode due to the surface tension of the mercury [4]. Iridium was used as the electrode

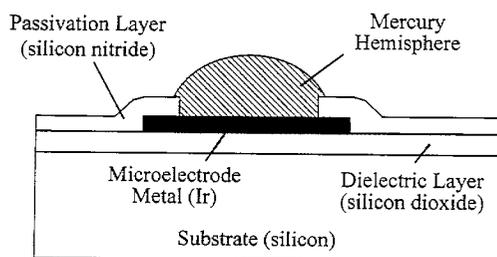


Fig. 3. Cross section of mercury hemisphere electrodeposited on an iridium microelectrode.

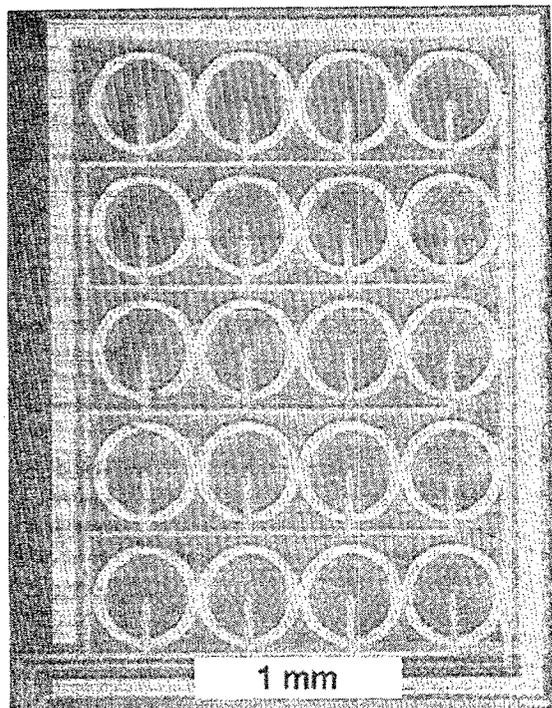


Fig. 4. Photograph of the electrochemical detector showing the reference electrodes (circles), the array of mercury working electrodes (inside the circles) and the counter electrode (wide path around the periphery.)

material due to its very low solubility in mercury [5]. A reference electrode of Ag/AgCl could be deposited onto an exposed electrode by electroplating silver followed by anodization. An on-chip iridium counter electrode is also provided (Fig. 4).

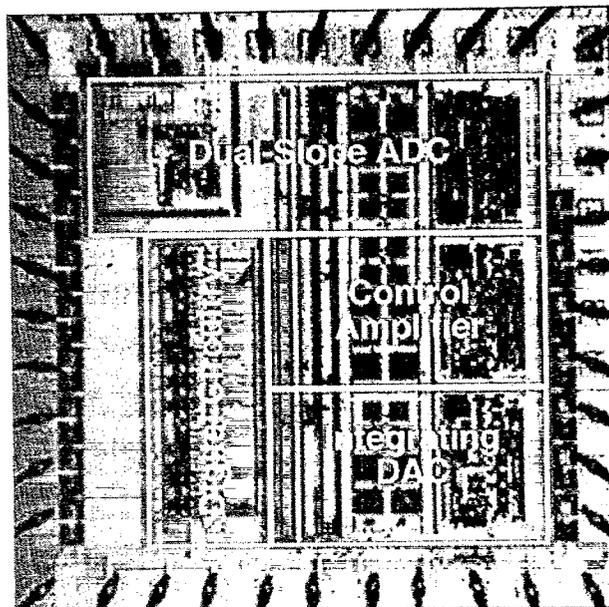


Fig. 5. Photograph of the integrated potentiostat.

5. System electronics

The integrated potentiostat (Fig. 5) is a high-performance full-custom mixed-signal chip with a D/A converter and control amplifier for setting the electrode potential, and a current-input A/D converter for digitizing the electrode current [6]. Differential switched capacitor circuitry is employed to minimize voltage gain and offset errors. The A/D converter is a digitally scaled integrating converter that can measure over eight decades of current with 13 bit accuracy. To supply DC currents and still be able to drive the large electrode capacitances, a custom

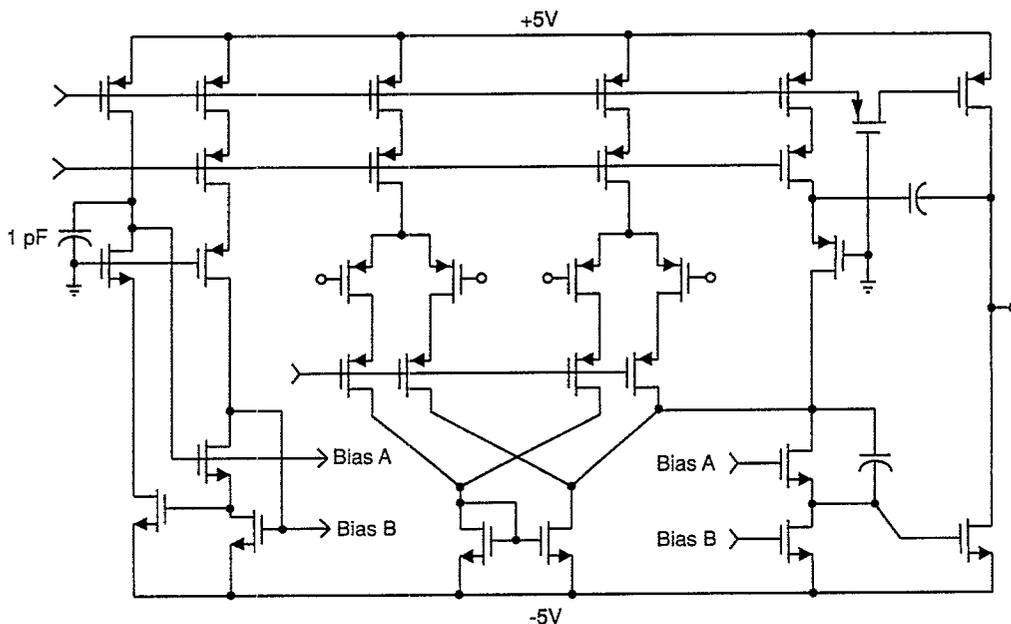


Fig. 6. Schematic of unconditionally stable amplifier circuit used to drive the electrodes.

amplifier was designed (Fig. 6). This circuit can drive the required electrode currents and is unconditionally stable for any capacitive load [7]. The 2×2 mm chip is fabricated in the Orbit Semiconductor $2 \mu\text{m}$ analog CMOS process.

The electrochemical detector and potentiostat chip are combined with a 68HC11 microcontroller to create a hand-held, battery powered analysis system. The microcontroller is programmed to control the analysis by interfacing to the potentiostat. The microcontroller controls the timing of the analysis, sets the D/A conversion values for the electrode potentials, and records the currents measured by the ADC. A UART built into the 68HC11 is used to transmit the current and voltage data to the serial port of a laptop computer, where the information is plotted and analyzed.

6. Experimental results

Experimental analyses performed with the system demonstrate excellent sensitivity and noise performance. An important feature of SWASV is the ability to control the sensitivity by setting the preconcentration time. A longer preconcentration leaves higher initial concentrations in the mercury electrode, thus increasing the peak height and therefore the sensitivity. Fig. 7 demonstrates this feature by plotting the measured stripping current for a 10 ppb lead solution for several preconcentration times. As expected, the current peak height, and thus the sensitivity is proportional to the preconcentration time.

A concern for many chemical sensors is repeatability over several uses. With this system, multiple measurements performed with the same electrode are repeatable, showing that the electrode is not limited to a single use (Fig. 8).

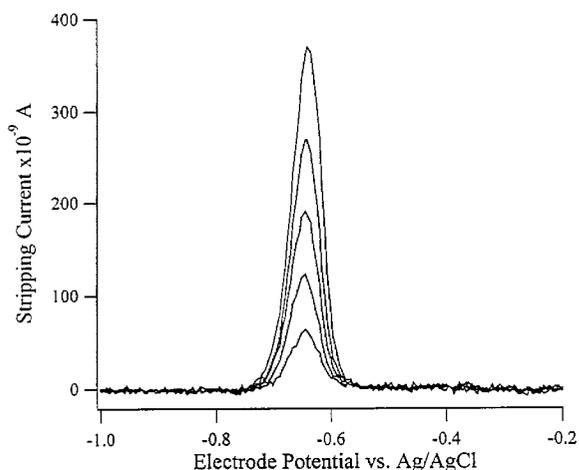


Fig. 7. Measured stripping currents for the mercury electrode array in a 8 mM HClO_4 solution with 10 ppb Pb^{2+} . The preconcentration times were 150, 300, 450, 600 and 750 s. The perchloric acid is added to control the solution pH.

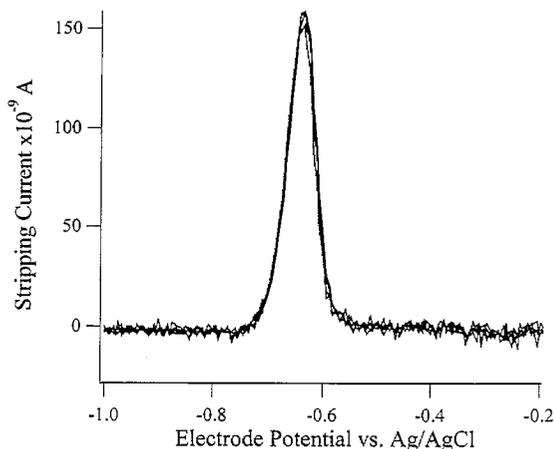


Fig. 8. Superposition of five successive analyses using the same electrode. The sample was an 8 mM HClO_4 solution with 10 ppb Pb^{2+} . The preconcentration time was 300 s.

The above graphs show results with laboratory prepared solutions with perchloric acid added to control the solution pH. To obtain a flat baseline and improve the dynamic range, baseline reference curves were measured. These baselines were measured by performing an analysis with no preconcentration time immediately after the actual stripping analysis. The baselines were used to subtract out currents due to background reactions such as oxygen reduction. The sensitivity of the system is better than 1 ppb, and even smaller concentrations can be detected with buffered solutions in the laboratory (Fig. 9). An EG&G 273A potentiostat was used for the electrode characterization analyses in Figs. 7–9.

Unmodified natural water samples can also be measured down to the 1 ppb level with the complete analysis system. Fig. 10 shows an analysis of a typical tap water

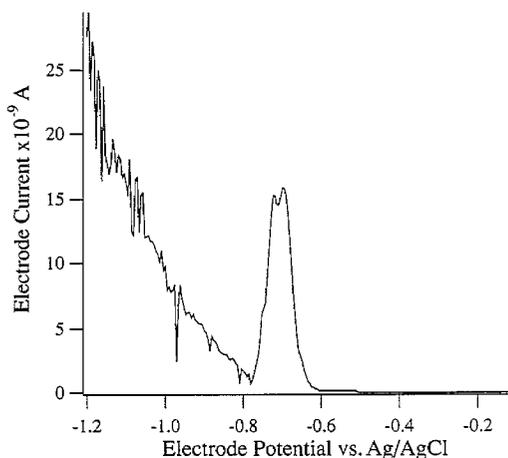


Fig. 9. Measured stripping currents for a 8 mM HClO_4 solution with 1 ppb Pb^{2+} . The preconcentration time was 600 s. The lead peak is clear against the background current, suggesting that concentrations below 1 ppb can be detected.

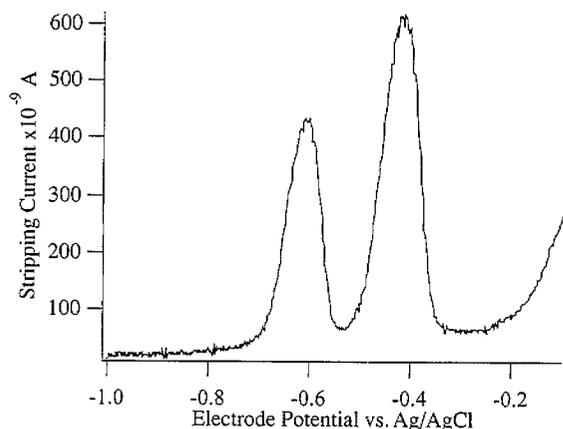


Fig. 10. Experimental analysis of unbuffered natural water containing about 25 ppb of Cd^{2+} and Pb^{2+} using the complete integrated sensor system.

sample, showing two clear peaks corresponding to about 25 ppb of Cd^{2+} and Pb^{2+} . The integrated potentiostat was used for this analysis and no baseline correction was performed.

7. Conclusions

We have demonstrated a miniaturized heavy metal analysis system having a detection limit of 1 ppb. The system components are a microfabricated mercury film electrode array, a high performance single chip potentiostat and a microcontroller. The system is currently being used to test drinking water, ground water and semiconductor processing fluids.

Acknowledgements

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Biographies

Richard Reay was born in Bellingham, WA in 1969. He received the B.S., M.S., and Ph.D. degrees in electrical engineering from Stanford University in 1991, 1992, and 1994, respectively. His graduate work was funded by National Science Foundation and A.R.C.S. Foundation Graduate Fellowships. His industrial experience includes internships at Linear Technology Corporation and Sumitomo Electric Ltd. In 1994–1995 he was a Research Associate at Stanford University, developing integrated sensors and circuits. He is currently a Research Staff Member at the I.B.M. Almaden Research Center working on magnetic recording technology.

Anthony Flannery was born in Philadelphia, PA in 1963. He received his B.A. in chemistry from Princeton University in 1986 and his M.S. in electrical engineering from Stanford in 1995. His industry experience includes the design of control for impulse capture systems, remote sensing units, and a novel gas mixing system. He is currently a Ph.D. candidate at Stanford researching applications of ultramicroelectrode arrays.

Christopher W. Stormont was born in Burbank, CA, in 1957. He received the B.S. degree in chemistry from the University of California, Riverside, in 1980, and the M.S. degree in material sciences from the University of Southern California, Los Angeles, in 1987. From 1980 to 1987, he was employed at the Hughes Aircraft Torrance Research Center and the TRW Advanced Microwave Circuits Department, working on process development for GaAs digital and analog microwave circuits. Between 1987 and mid-1993, he worked at the Palo Alto Veterans Administration Rehabilitation Research and Development Center developing fabrication techniques for use in the neural interface project (at Stanford). He recently joined the Department of Electrical Engineering at Stanford University, where he is a Research and Development Engineer. He is active in co-advising students on several other solid-state transducer projects in Dr. Kovacs' laboratory at Stanford University.

Samuel P. Kounaves was born in Anaconda, Montana, in 1948. He received a B.S. and M.S. degrees in Chemistry from California State University at San Diego, in 1975 and 1978 respectively, and the Ph.D. degree from the Université de Genève, Switzerland, in 1985. After a Post-doctoral studies at S.U.N.Y. Buffalo (1985–1986) and

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Gregory T.A. Kovacs was born in Vancouver, British Columbia, in 1961. He received the B.A.Sc. degree in Electrical Engineering from the University of British Columbia, Vancouver, B.C., in 1984, the M.S. degree in Bioengineering from the University of California, Berkeley, in 1985, the Ph.D. degree in Electrical Engineering

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