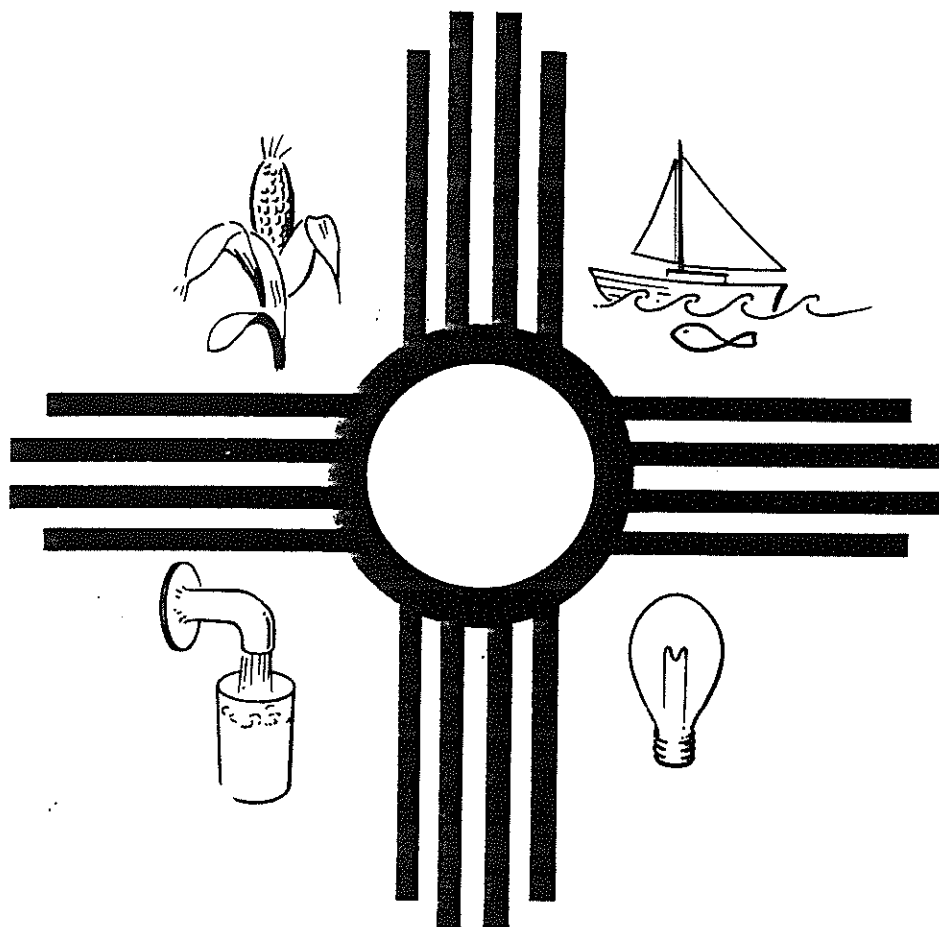


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NEW APPROACHES TO METAL SPECIATION IN NATURAL WATERS BASED ON MODIFIED AND MICROVOLTAMMETRIC ELECTRODES

A Summary Report
Project Number 1345671



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**NEW APPROACHES TO METAL SPECIATION
IN NATURAL WATERS BASED ON MODIFIED
AND MICROVOLTAMMETRIC ELECTRODES**

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in cooperation with

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ABSTRACT

The proliferation of heavy-metal contaminants in water has focused attention on their determination and characterization. The challenging research field of metal speciation (or the identification of a metal species) in natural waters, is in its early stages and numerous problems remain. This project resulted in more effective, reliable tools for speciation analysis of natural waters, thus offering a better understanding of the presence, toxicity, and transport of trace metals. Results could be included in future water quality legislation and used for measuring speciation-related water quality parameters.

Specifically, advanced electrode technology was developed to overcome the organic-adsorption problem. Overcoming this problem allows for speciation studies in non-saline waters, like much of the water in New Mexico. Results also offered new information on size distribution of metal species, and expanded the technology toward additional trace elements.

Key words: speciation, trace metals, water measurements, toxicity, water quality, heavy metals

PREFACE

Unlike other final technical completion reports published by the WRRI, this report constitutes a brief synopsis of the institute supported project entitled "New Approaches to Metal Speciation in Natural Waters Based on Modified and Microvoltammetric Electrodes" under the direction of Dr. Joseph Wang. The purpose of this report is to bridge the gap in understanding between the analytic chemist and practicing water quality professionals in the field. A summary of trace metal analysis, new accomplishments derived from this project, and use of these results is contained herein. The reader is urged to review the numerous journal articles published in conjunction with this project for additional information on specific points of interest. Articles are referenced throughout the report and reprints are available through the institute or from Dr. Wang. Those interested in learning more about the technique and or receiving training in stripping analysis should contact Dr. Wang, Department of Chemistry, New Mexico State University, Las Cruces, New Mexico, 88003.

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INTRODUCTION

The New Mexico Water Resources Research Institute has supported research efforts of Dr. Joseph Wang of New Mexico State University's Chemistry Department for several years. The research analyzes trace metals in water samples for understanding their toxicity. From 1982 to 1984, Dr. Wang conducted a study entitled, "New Approaches for On-Line Stripping Analysis of Trace Metals." The objective of this study was to develop a real-time analytical technique for analysis of heavy metals in water. An electrochemical technique was developed through this project.

In 1987, the institute began its support of Dr. Wang's effort to produce more effective and reliable tools for analysis of natural waters, resulting in a better understanding of their toxicity and transport of trace metals. The results of the two-year project are described briefly here. The reader is encouraged to review the numerous publications which resulted from this research. The following four journal articles were derived from the research:

Improved Anodic Stripping Voltammetric Measurements of Silver by Codeposition with Mercury, Joseph Wang, Ruiliang Li, and Huang Huiliang, Electroanalysis, 1989:1:417-421.

Anodic-Stripping Voltammetry of Heavy Metals in the Presence of Organic Surfactants, Waldyslaw W. Kubiak and Joseph Wang, Talanta, 1989:36:821-824.

Anodic Stripping Voltammetry at Ultramicroelectrodes for Metal Speciation Studies in Aqueous Solutions of Low Ionic Strength, Joseph Wang and Javad M. Zadeii, J. Electroanal. Chem., 1988:246:297-305.

Accumulation and Voltammetric Measurement of Silver at Zeolite-Containing Carbon-Paste Electrodes, Joseph Wang and Teddy Martinez, Analytica Chimica Acta, 1988:95-102.

To understand the work of Dr. Wang and his colleagues, the technique of trace metal analysis is described below. A complete and understandable description of the technique is contained in Dr. Joseph Wang's book entitled, *Stripping Analysis Principles*,

Instrumentation, and Applications, published in 1985 by VCH Publishers. The description below was extracted from Dr. Wang's book. Following the basic concepts of trace metal analysis is a brief summary of the accomplishments and uses resulting from this project.

TRACE METAL ANALYSIS

Many heavy metals are toxic, dangerous pollutants second only to pesticides in environmental importance.¹ Perhaps the most important feature distinguishing metals from other toxic pollutants is that metals are not biodegradable and may persist for a long time.² The most hazardous and important heavy metals are lead, mercury, cadmium, arsenic, thallium, and selenium. Some of these have been linked to cancer and heart diseases.³

Some metals that are essential nutrients such as copper, zinc, or tin can be toxic, depending on their concentration levels. For these metals, there exists a fine line between toxic and essential levels. Consequently, reliable knowledge of the metal content is crucial. An understanding of the chemical state of trace metals in natural waters or fluids is important in determining their reactivity, transport, and toxicity. The potential toxicity of a metal is controlled to a great extent by its physical and chemical (physicochemical) form. Speciation studies are those that determine the individual physicochemical forms of the metal. These studies are required for understanding the role trace metals play in natural waters or human health.⁴

A thorough understanding of the effects of trace metals depends largely on the availability of sensitive and reliable analytical techniques. Various techniques used include atomic absorption, plasma emission and x-ray fluorescence spectroscopy, stripping analysis,

¹Ellis, W. D. 1973. J. Chem. Educ. 50:A131.

²Florence, T.M. 1982. Talanta. 29:345.

³Dulka, J.J., and T. H. Risby. 1976. Anal. Chem. 48:640A.

⁴Wang, J. 1985. Stripping Analysis Principles, Instrumentation, and Applications. VCH Publishers, Inc.: Deerfield Beach.

or neutron activation. Factors such as detection limits, instrumentation costs, analysis time, and sample preparation or selectivity, adsorption losses, contamination or disruption of equilibrium, should be considered when determining a specific technique for trace metal analysis.

Stripping Analysis

Stripping analysis allows for the simultaneous measurement of four to six trace metals at concentration levels down to parts per billion, utilizing inexpensive instrumentation. Only flameless atomic absorption has nearly the same sensitivity, but at a much higher cost. Other techniques such as inductively coupled plasma atomic emission spectroscopy and neutron activation analysis have even higher instrumentation costs.⁵

Reliable and versatile stripping instruments are available for \$5,000 to \$8,000. The instrument is small, has very low power demand, and requires no special installation, such as cooling or ventilation. No additional equipment or analysis time is required for multielement stripping measurements. No other technique can compete with stripping analysis on the basis of sensitivity per dollar invested.⁶

Through careful stripping analysis experiments it is possible to determine the exact chemical nature of the trace element. Another advantage is its suitability for automatic on-line monitoring and for in situ measurements. The main limitation of stripping analysis is its restriction to about 30 metals (Ag, As, Au, Ba, Bi, Cd, Co, Cs, Cu, Ga, Ge, Hg, In, K, Mg, Mn, Na, Ni, Pb, Pt, Rb, Rh, Sb, Se, Sn, Sr, Tc, Te, and Zn).⁷

⁵Ibid.

⁶Ibid.

⁷Ibid.

How Stripping Analysis Works

Stripping analysis evolved from the early electrochemical experiments of Zbinden⁸, who planned a two-stage quantitative determination of copper in solution by first electroplating it onto a platinum electrode, and then weighing the mass of copper deposited. However, since the resulting copper was too small to weigh accurately, he decided instead to make the quantitative determination by measuring the electric current required to drive the copper metal back into solution, thus "stripping" the metal from the electrode on which it had been deposited. Modern stripping analysis retains the same two-stage character.

The first stage of deposition by reduction of metal ions at a negative electrode accomplishes a very great "preconcentration" of the analyte (that which is to undergo analysis). In the second stage, the voltage or potential of the electrode is reversed to the point that the deposited metal undergoes reoxidation, and is thus electrolyzed back into solution as metal ions. The electric current associated with this dissolution of the metal deposit provides a direct linear measure, by Faraday's fundamental law of electrolysis, of the mass of metal removed from the electrode. The combination of these two steps in the analysis technique yields great sensitivity, and a strong signal to noise ratio that is characteristic of stripping analysis.

The stripping analysis methodology outlined above is referred to as anodic stripping voltammetry (ASV). As we have seen, it is characterized by the concentration of trace metals by reduction into or onto an electrode, followed by anodically reoxidizing (stripping) them to produce an electric current which is a function of the applied potential. The

⁸Zbinden, C. Bull. Soc. Chim. Biol., 1931, 13,35.

electrode's reduction or oxidation strength is controlled by the applied potential. For example, as the potential of the electrode becomes more negative (cathodic), the electrode becomes a stronger reductant (electron source). Therefore, assuming an electroactive species is present, a current will be recorded when the applied potential becomes sufficiently negative or positive for it to be electrolyzed. The resulting current is recorded on a voltammogram, which displays current (vertical axis) versus potential or voltage (horizontal axis). Depending on the nature of the measurement, a wave or peak-shaped response may be observed. By careful interpretation of the voltammogram, important information (analytic, mechanistic, kinetic, or thermodynamic) is obtainable.

Details of the Stripping Process

Electrodes: Anodic stripping measurements are carried out in an electrochemical cell, which is usually a covered beaker of glass, quartz, or Teflon. The cell material is chosen to reduce errors from contamination and adsorption. The cell contains three electrodes (working, reference, and auxiliary), which are immersed in the sample solution. The working electrode is the electrode at which the reaction of interest occurs. Generally, it is characterized by its small surface area, which enhances polarization. Another reason for using very small electrodes is to minimize depletion of the analyte. Micromercury electrodes are usually used. Solid electrodes made of gold, carbon, or platinum are used for determining of metals with oxidation potentials more anodic than that of mercury. The reference electrode provides a known and stable potential that is insensitive to the composition of the solution under study and with which the potential of the working electrode is compared. Because of its constant composition the reference electrode remains

unpolarized during the analysis.

To minimize errors from cell resistance in controlling the working electrode's potential, a third electrode - the auxiliary electrode - is usually employed. This electrode is made of a chemically inert conducting material with a reasonable surface area. Platinum wires or graphite rods are the most often used auxiliary electrodes.

Supporting Electrolyte: The sample for stripping analysis must be a solution. If the sample is a solid, it must be dissolved. Deriving the equations for the peak current demands minimizing electrical migration of the metal ion caused by the electric field. To accomplish this, an inert supporting electrolyte is introduced in the sample solution, which lowers the transference number of the ions measured to virtually zero. This also insures the conductive medium that voltammetry requires. The supporting electrolyte may be an inorganic salt, a mineral acid or a base. Samples with high salt content, like sea water, do not require addition of supporting electrolytes. The ideal electrolyte should give well-separated and well-shaped peaks for all the metals sought. The concentration of the supporting electrolyte is usually about 0.1 M, a compromise between high conductivity and minimum contamination.

Oxygen Removal: Because dissolved oxygen interferes with stripping analysis, it must be removed from the sample solution. The most frequently used method for removing oxygen consists of bubbling a gas, like nitrogen or argon, through the solution.

Deposition Step: Usually the preconcentration is done by cathodic (the negative terminal of an electrolytic cell) deposition at a controlled potential (more negative than the reduction potential of the element or elements to be measured). The metal ions reach the

electrode surface by diffusion and convection -- forced by rotating the working electrode or stirring the solution -- where they are reduced and concentrated as amalgams (alloys of mercury with another metal) in the mercury. The duration of the deposition step is selected according to the concentration level of the metal ions in question: from less than 1 minute at the 0.1-ppm (0.1-mg/l) level to about 10 minutes at the 1-ppb (1-ug/l) level.

Current/Potential Voltammogram: Following the preselected time of the deposition step, the potential is scanned anodically (toward more positive potentials), linearly, or in a more sensitive potential vs. time waveform. During this scan, the amalgamated or combined metals are stripped out of the electrode in an order that is a function of each metal's standard potential, are reoxidized, and give rise to anodic peak currents that are measured. The result is the current/potential voltammogram providing the analytical information of interest. The peak potential of each metal is characteristic of that metal and is related to the standard potential of its oxidation/reduction. The peak current is proportional to the concentration of the corresponding metal ion in the test solution. The concentration is determined by a standard addition or a calibration curve.

Disadvantages of Anodic Stripping Voltammetry

The main types of interferences in ASV are overlapping stripping peaks and intermetallic compound formation. Overlapping peaks, caused by similarity in oxidation potentials, cause problems in simultaneous determination of lead with tin, thallium with cadmium, or bismuth with antimony.

The formation of intermetallic compounds in or on the working electrode may affect the size or position of the peak current for a particular metal. For example, the deposition of zinc and copper in mercury results in such a mutual interference. This type of problem

may be avoided or minimized by using the hanging mercury drop electrode rather than a thin mercury film electrode (in which this problem is more severe), by the addition of a third element that preferentially combines with one of the metals in question, or by using a deposition potential at which one of the ions is not plated.

To obtain accurate and reproducible results, adequate attention must be paid to certain key elements. Analysts are working with extremely dilute solutions. All procedures of trace analysis practice, such as sample handling, preparation and storage of standards, glassware and reagent purity, clean bench working, and so on, must be observed to minimize errors caused by contamination, adsorption losses, and alterations of the dissolved trace metal levels.

A particular problem with ASV is the adsorption of organic matter on the electrode surface which affects the reliability of ASV speciation work. Another problem, that of high ionic strength restriction, or the need for electrolytes of sufficient strength, limits its utility in nonsaline natural waters.

Anodic stripping voltammetry has been used extensively to analyze natural water samples. Ariel and Eisner used ASV, in one of its early (1963) environmental applications, to analyze zinc, cadmium, and copper in the Dead Sea brine.⁹ Much of the success in applying ASV for analyzing natural waters is attributed to Florence, who used ASV about 10 years ago to determine trace levels of lead, cadmium, zinc, copper, thallium, bismuth, indium, and antimony in the Pacific Ocean, as well as in fish, seaweed, abalone, and oysters inhabiting the water.¹⁰

⁹Ariel, M., and E. Eisner. 1963. J. Electroanal. Chem. 5:362.

¹⁰Florence, T.M. 1972. J. Electroanal. Chem. 35:237.

THE CURRENT RESEARCH

The objective of the current work is to develop new stripping voltammetric schemes based primarily on advanced working electrode technology. Such schemes would overcome some of the major problems associated with trace metal speciation studies using stripping voltammetry including the problem of ionic strength restrictions and surface contamination. Besides addressing these problems, the newly developed methods have proven to be faster, simpler, and less prone to contamination risks.

Ultramicroelectrodes: This study confirmed the suitability and advantages of ultramicroelectrodes for speciation work in waters of low ionic strength, or having insufficient electrolytes. Because of these tiny electrodes, more accurate peak potentials were measured resulting in more reliable speciation data.

Water with Low Salt Content: Application of stripping voltammetry to speciation studies have been concerned primarily with marine samples, which contain high ionic-strength electrolyte.¹¹ The high ionic-strength electrolyte insures a conductive medium sufficient that potentials applied to the working electrode are not ohmically lost in the bulk solution.¹² Low ionic strength occurs in water with low salt content as is true of New Mexico water. Most inland water systems containing negligible ionic-strength electrolyte require the addition of supporting electrolyte. In speciation work, such addition is accompanied by severe errors due to disturbances of natural ionic equilibria and contamination. If on the other hand, one uses the conventional electrodes in non-saline

¹¹Wang, J. and J. Zadeii. 1988. J. Electroanal. Chem. 246:297-305.

¹²Ibid.

water samples--without supporting electrolyte--one risks complications due to the uncompensated solution resistance and the resultant distorted voltammograms. Low ionic-strength electrolytes cause what are referred to as ohmic losses. Minimizing resistance effects or ohmic losses have pronounced effects upon the peak characteristics used for obtaining the speciation data. This research confirmed the suitability of ultramicroelectrodes for anodic stripping studies of low-ionic strength water samples.

Chemically Modified Electrodes: In recent years, there has been considerable interest in chemically modified electrodes. New preconcentrating electrodes of potential use in water analysis were designed and evaluated in this part of the project. Substantial effort has been devoted to the development of sensor bases on chemically modified electrodes (CMEs). One of the most promising avenues involves the use of CMEs first to preconcentrate the analyte at the electrode surface and then quantify the analyte by conventional voltammetric methods.¹³ This would extend the range of stripping voltammetry toward analytes that can not be accumulated by electrolysis. Modifying the surface is commonly done by mixing the preconcentration agent into a carbon-paste matrix. This research studied a method for preconcentration based on zeolite-modified electrodes. Zeolites have attracted attention for several decades because of the favorable ion-exchange processes of zeolites. Zeolites were used as surface-modifiers for selective measurements of silver, and an effective silver sensor was obtained. Similar results were also obtained with tropolone-modified electrodes for measurements of tin.¹⁴

¹³Wang, J. and T. Martinez. 1988. Anal. Chim. Acta. 207:95:102.

¹⁴Wang, J. et al. 1989. Anal. Lett. 22:719-727.

Measurements of Free Silver Ion: Recent studies have demonstrated that measurements of total silver cannot provide an accurate assessment of its environmental impact of this metal, and that silver speciation is an essential factor in its toxicity in water. Thus, it is not the silver concentration in water that is so crucial, but the species of silver, some being much more toxic than others. Wang and his colleagues developed an effective stripping procedure for monitoring trace levels of silver using of low (20 parts-per-billion) levels of mercury.¹⁵ The use of low mercury concentration results in a very small mercury peak that actually improves the base line of the silver response. Consequently, there is significantly higher sensitivity, sharper peaks, and improved reproducibility compared to studies not using mercury. This technique was applied to river-water samples.

Interference from Surface-Active Substances: ASV is subject to interferences from surface-active (or surfactants) substances in the sample. Various approaches have been suggested for minimizing or eliminating these interferences including the removal or destruction of organic matter by using ultraviolet irradiation,¹⁶ or ozone oxidation.¹⁷ Surface-active substances have a marked effect on ASV because of their adsorption at the electrode surface. Effects include lower and broader stripping peaks, and shifts in peak potentials. These effects greatly complicate the interpretation of ASV data.¹⁸

This research tackled the surfactant problem based on the use of fumed silica. The

¹⁵Wang, J., R. Li, and H. Huiliang. 1989. Electroanalysis. 1:417-421.

¹⁶Batley, G.E. and Y.J. Farrar. 1978. Anal. Chim. Acta. 99:283.

¹⁷R.G. Clem and A.T. Hodgson. 1978. Anal. Chem. 50:102.

¹⁸Kubiak, W. W. and J. Wang. 1989. Talanta. 36:8:821-824.

adsorptive properties associated with silica were used to remove large surfactants from the bulk solution. The fumed silica acts as a rapid cleanup of a wide variety of large organic compounds from aqueous solutions. The addition of silica is an extremely fast, simple, low cost, and effective approach to eliminating surfactant interferences as demonstrated in this project.

CONCLUSIONS AND RECOMMENDATIONS

Wang sought to overcome some the problems associated with anodic stripping voltammetry. Several strategies were successfully explored including the use of new chemically modified electrodes, ultramicroelectrodes, and stripping techniques. New preconcentrating modified electrodes such as zeolite, pectic acid, and tropolone were designed to analyze silver, lead, and tin, respectively. The significant reduction of resistance effects attributable to water of low ionic strength came about through the use of microelectrodes. The ability to simultaneously measure two to three trace metals using an adsorptive approach was illustrated. The use of fume-silica eliminating surface adsorption problems in stripping measurements was also demonstrated.

These new developments greatly enhance the power of stripping voltammetry and offer new tools for trace measurements and speciation work in natural waters. Because the determination of trace metal speciation in natural waters is a challenging task due to very low concentrations of these metals, procedures such as those designed by this study allow for more effective, accurate measurements. Technicians in the field should consider stripping voltammetry for addressing their needs. New versions of the technique, based on adsorptive accumulation of metal chelates, greatly enhance the scope of stripping voltammetry toward numerous trace elements.

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